GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: 2/10/79

Project Title: Synthesis and Synthetic Applications of Organometallic Compounds

Project No: G-33-644 Green card

Project Director: Dr. E. K. Barefield

Sponsor: National Science Foundation, Washington, D. C. 20550

Agreement Period: From 1/1/79 Until ~~6/30~~ 12/31/81* 81*
*Includes 6 month flexibility period

Type Agreement: Grant No. CHE-7818584

Amount: $64,200 NSF Funds (G-33-644)
9,063 GIT Contribution (G-33-336)
$73,263 Total

Reports Required: Annual Progress Reports; Final Project Report

Sponsor Contact Person (s):

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Defense Priority Rating: n/a

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GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION SHEET

Date 6/29/83

Project Title: Synthesis and Synthetic Applications of Organometallic Compounds

Project No: G-33-644

Project Director: Dr. E. Kent ~~Barfield~~ Barefield

Sponsor: National Science Foundation

Effective Termination Date: 12/31/81

Clearance of Accounting Charges: 12/31/81

Grant/Contract Closeout Actions Remaining:

- [ ] Final Invoice and Closing Documents
- [X] Final ~~Fiscal~~ Accounting Report (FCTR)
- [X] Final Report of Inventions
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- [ ] Other _____

NOTE: Information received 6/83 indicates final report was mailed 3/30/82. This action is to close account on an old project.

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G-55-644

APPENDIX VI

NATIONAL SCIENCE FOUNDATION Washington, D.C. 20550	FINAL PROJECT REPORT NSF FORM 98A	

PLEASE READ INSTRUCTIONS ON REVERSE BEFORE COMPLETING

PART I–PROJECT IDENTIFICATION INFORMATION

1. Institution and Address	2. NSF Program	3. NSF Award Number
Georgia Institute of Technology Atlanta, GA 30332	Syn. Inorg. Organomet.	CHE-7818584
	4. Award Period From 1/1/79 To 12/31/81	5. Cumulative Award Amount $64,200

6. Project Title

Synthesis and Synthetic Applications of Organometallic Compounds

PART II–SUMMARY OF COMPLETED PROJECT *(FOR PUBLIC USE)*

This research was concerned with the synthesis of new organometallic compounds that were designed to test existing theories of bonding and/or chemical reactivity and with the development of new synthetically useful applications of organometal reagents. Attention was focussed on reactions of electrophilic organic reagents such as iminium and nitrilium salts and α-halothioethers with low-valent metal complexes and with the synthesis and reactivity of the novel, paramagnetic cyclopentadienyl-bis(ligand)nickel(I) complexes. In the former area a number of new organometallic compounds were synthesized and characterized (including five single crystal structure determinations). Both self-coupling reactions of iminium salts and cross-coupling reactions with alkyl halides of potential synthetic utility were developed as were nickel based reagents for formation of three-membered rings from olefins. In the latter area reactions of well-known compounds such as nickelocene and bis(cyclopentadienylnickel carbonyl) were found to involve previously unrecognized nickel(I) intermediates. Several examples of this type of compound were synthesized and studied. Establishment of the identity of these species is expected to have a significant impact on the development of future chemistry of cyclopentadienylnickel species.

PART III–TECHNICAL INFORMATION *(FOR PROGRAM MANAGEMENT USES)*

1. ITEM *(Check appropriate blocks)*	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM	
				Check (✓)	Approx. Date
a. Abstracts of Theses		X			
b. Publication Citations		X			
c. Data on Scientific Collaborators		X			
d. Information on Inventions	X				
e. Technical Description of Project and Results		X			
f. Other *(specify)*					

2. Principal Investigator/Project Director Name *(Typed)*	3. Principal Investigator/Project Director Signature	4. Date
E. Kent Barefield		26 Mar.1982

NSF Form 98A (5-78) Supersedes All Previous Editions

Form Approved OMB No. 99R0013

Part III - Technical Information

1a. Theses (abstracts attached)

(1) Dennis J. Sepelak, Ph.D., 1980. "Organometallic Chemistry of Iminium Salts."

(2) Allen M. Carrier, Ph.D. Thesis, 1981. "Some Organometallic Chemistry of Iminium and Nitrilium Salts."

1b. Publication Citations (copies of papers attached)

(1) "Organometallic Chemistry of Carbon-Nitrogen Multiple Bonds II. Reactions of Cyclopentadienylirondicarbonyl Anion with Iminium Salts; Chemistry of the Products," E. K. Barefield and D. J. Sepelak, J. Am. Chem. Soc., 101, 6542 (1979).

(2) "Organometallic Chemistry of Carbon-Nitrogen Multiple Bonds III. Reaction of Tris(triphenylphosphine)platinum(0) with Dimethylmethyleneiminium Chloride: X-Ray Structures of the Products $[(Ph_3P)\overset{\bullet}{P}tCH_2N(CH_3)_2\overset{\bullet}{C}H_2N(CH_3)_2(C\ell)]C\ell$ and cis-$\{(Ph_3P)Pt[CHN(CH_3)_2]C\ell_2\}$, "E. K. Barefield, A. M. Carrier, D.J. Sepelak and D. G. Van Derveer, Organometallics, 1, 103 (1982).

(3) "Cyclopentadienylbis(ligand)nickel(I): Synthesis and Characterization, Including the X-ray Structure of η^5-Cyclopentadienyl-1,1'-bipyridylnickel(I). Observations on the Mechanism of Substitution of Nickelocene," E. K. Barefield D. A. Krost, D. S. Edwards, D. G. Van Derveer, R. L. Trytko and S. P. O'Rear, J. Am. Chem. Soc., 103, 6219 (1981).

(4) "Cyclopentadienylbis(ligand)nickel(I): Synthesis, Characterization and Reactivity," E. K. Barefield, D. A. Krost, R. Trytko, S. Edwards, S. O'Rear and A. N. Williamson, Biennial Inorganic Chemistry Symposium, Guelph, Canada, 1980.

(5) "Cyclopentadienylbis(ligand)nickel(I): Synthesis, Characterization and Reactivity," E. K. Barefield, NSF National Organometallic Chemistry Workshop, Northwestern University, 1980.

(6) "Organometallic Chemistry of Carbon-Nitrogen Bonds. Products Derived from Reactions of Tris(Triphenylphosphine)Platinum(0) with Iminium Salts," E. Kent Barefield, Allen M. Carrier and D. G. Van Derveer, 181st ACS National Meeting, Atlanta, Ga., Abstract INOR 66 (1981).

(7) "Coupling of Iminium and Nitrilium Salts Using Metal Complexes as Two Electron Reagents," E.K. Barefield and A. M. Carrier, 1981 Joint Central and Great Lakes Regional ACS Meeting, Dayton, Ohio. Abstract INOR 199.

1c. Scientific Collaborators

Alex N. Williamson, Assistant Professor, Department of Chemistry, North Carolina State A&T University.

Don G. Van Derveer, Research Scientist, Georgia Tech.

Dennis J. Sepelak, graduate student, Georgia Tech.

Allen N. Carrier, graduate student, Georgia Tech.
David A. Krost, graduate student, Georgia Tech.
James Davidson, graduate student, Georgia Tech.
Paul McCarten, graduate student, Georgia Tech.
Shaun O'Rear, undergraduate student, Georgia Tech.
Rodney Trytko, undergraduate student, Georgia Tech.
Scott Edwards, undergraduate student, Georgia Tech.
Jacqueline Davidson, 1980 URP student, Georgia Tech.

1d. Inventions

None

1e. Technical Description of Project and Results.

Research during this grant period was conducted in two areas: I. Organometallic Chemistry of Carbon-Nitrogen Multiple Bonds and II. Chemistry of Nickel (I). In the former area attention was focused on a) reactions of $CpFe(CO)_2^-$ with iminium salts, b) reactions of $(Ph_3P)_3Pt$ with iminium salts, c) reductive coupling of iminium salts using nickel(0) reagents and d) reactions of two electron organometallics with nitrilium salts, e) related chemistry involving $ClCH_2SR$ as electrophiles. In the latter area, preliminary investigations were made on cyclopentadienylbis(ligand) nickel(I) complexes. Results of work completed in areas Ia-c and II are amply described in the attached copies of published papers and thesis abstracts. The work in area II serves as preliminary work for our continuation proposal. Areas Id and Ie deserve some additional comment.

Id. In addition to the work on Cp_2V - nitrilium salt chemistry described in Carrier's thesis abstract we have examined reactions of $Cp_2Ti(CO)_2$ with nitrilium salts. This work has proceeded slowly because of some unfortunate difficulties in the preparations of the titanium reagent but it is now clear that two products of stoichiometry Cp_2Ti: 1 nitrilium salt and Cp_2Ti: 2 nitrilium salt can be isolated. These are currently being characterized. So far attempts to electrochemically couple nitrilium salts have failed.

Ie. In my request for a no-cost 6 month extension of this grant I indicated that studies on $[CpNi(L)CH_2SR]$ and $[CpNi(L)CH_2SR_2]^{+1}$ were to be undertaken.

Objectives were to develop new alkylnickel chemistry and new cyclopropanation reagents. This work has progressed very well and a number of very interesting results have been obtained.

The only example of the above complexes that was known at the time of my extension request was $CpNi(PPh_3)CH_2SPh$. We have developed syntheses of $CpNi(PPh_3)CH_2SCH_3$ (two routes) and salts of $[CpNi(PPh_3)CH_2S(CH_3)R]^{+1}$ (R = CH_3, Ph) and the dinuclear complex $\{[CpNi(PPh_3)CH_2]_2SCH_3\}^{+1}$ (single crystal X-ray structure completed). In the course of this work oxidative addition reactions of $RSCH_2Cl$ with $(Ph_3P)_3Ni$ have been examined. Trans-$(Ph_3P)_2Ni(C\ell)CH_2SR$ (R = CH_3, Ph) were obtained in good yield when the reactions were conducted at -20°C in ether (but not other solvents). The former complex converted to $(Ph_3P)Ni(C\ell)(\eta^2\text{-}CH_2SCH_3)$ in THF thus demonstrating a parallel between chemistry of $ClCH_2SCH_3$ and imininum salts.

The above nickel sulfur ylide complexes serve as cyclopropanation reagents although their poor solubility characteristics make them less useful than Helquists $[CpFe(CO)_2CH_2S(CH_3)_2]^{+1}$ reagents (JACS, 101, 6473 (1970). Studies in this area are continuing. In particular, questions concerning the stability of the $CpNi(PPh_3)CH_2^+$ ion will hopefully be answered when we complete our studies on the $-CH_2OCH_3$ complex which has just been synthesized. A full description of these results will appear in James Davidson's Ph.D. thesis and future publications.

SOME ORGANOMETALLIC CHEMISTRY OF IMINIUM AND NITRILIUM SALTS

A DISSERTATION

Presented to

The Faculty of the Division of Graduate Studies

By

Allen Mark Carrier

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

in the School of Chemistry

Georgia Institute of Technology

August, 1981

SUMMARY

Recent investigations have shown the possibility of an extensive chemistry between organometallic reagents and iminium and nitrilium salts. This work was undertaken with interest in 1) the reaction pathways involved in forming the electrophile-organometal species, 2) the modes of bonding of these unsaturates in the metal products, 3) the reactivity of the metal cation species and 4) developing synthetically useful metal assisted reactions of these electrophiles.

Iminium salts react with nickel tetracarbonyl to form products whose identity is solvent dependent. When dimethylmethyleniminium halides are treated with excess nickel carbonyl in tetrahydrofuran, an orange crystalline complex was isolated whose analytical data were consistent with the formulation $\{(CO)Ni[CH_2N(CH_3)_2]X\}$ (X = Cℓ, Br, I). The compounds were assumed to contain a dihapto iminium moiety and this was confirmed by an X-ray crystallographic examination of the bromide complex. Crystal data for $\{(CO)Ni[\eta^2\text{-}CH_2N(CH_3)_2]Br\}$ are: space group, Pnma; a = 7.376(1) Å, b = 7.783(3) Å, c = 13.127(6) Å; ρ_{calcd} = 1.99 g cm^{-3}, ρ_{exptl} = 1.90 g cm^{-3}; Z = 4. The Ni-L distances are: Ni-Br = 2.337(2) Å, Ni-C (iminium) = 1.91(1) Å, Ni-N = 1.955(9) Å, Ni-C (carbonyl) = 1.77 Å. An analogous complex was prepared with $[CH_2{=}N(CH_2C_6H_5)_2]Br$ and shown to exist in the dihapto form in solution.

When iminium salts are treated with excess nickel carbonyl in acetonitrile reductive coupling producing tetrasubstituted ethyl-

enediamines in low to moderate yields occurs. This iminium ion coupling reaction proceeds through $\{(CO)Ni[\eta^2\text{-}CH_2N(CH_3)_2]Br\}$ as inferred by the initial solution color. Thus coordination of the iminium ion to nickel results in its transformation from an electrophile to a nucleophile. This umpolung was shown to be general, with $\{(CO)Ni[\eta^2\text{-}CH_2N(CH_3)_2]Br\}$ reacting with a variety of organic halides giving coupled products in low to moderate yields.

Tristriphenylphosphineplatinum(0) reacts with $[CH_2{=}N(CH_3)_2]Cl$ in THF to yield $\{(Ph_3P)\overline{PtCH_2N(CH_3)_2CH_2N(CH_3)_2(Cl)}\}Cl$ which may be considered a complex of the bidentate ylide ligand $\bar{C}H_2\overset{+}{N}(CH_3)_2CH_2N(CH_3)_2$. When heated in acetonitrile, the chelate complex converts quantitatively to the carbene compound <u>cis</u>-$\{(Ph_3P)Pt[CHN(CH_3)_2]Cl_2\}$ ($\nu_{C=N}$ = 1611 cm^{-1}) and $(CH_3)_3N$. This decomposition is dependent upon the presence of a coordinating anion as shown by the stability of $\{(Ph_3P)\overline{PtCH_2N(CH_3)_2CH_2N(CH_3)_2(Cl)}\}BF_4$ in CH_3CN. Single crystal X-ray crystallographic studies were performed on both the chelate and carbene complexes. Crystal data for the chelate complex are: space group, $P2_1/c$; a = 13.86(1) Å, b = 8.933(2) Å, c = 19.52(1) Å; β = 98.65(6)°; ρ_{calcd} = 1.791 g cm^{-3}, ρ_{exptl} = 1.77 g cm^{-3}; Z = 4. This complex has Pt-L distances of: Pt-P = 2.223(2) Å, Pt-Cl = 2.362(2) Å, Pt-N = 2.134(4) Å, Pt-C = 2.017(5) Å. The platinum carbon distance is the shortest presently known for an sp^3 carbon (without fluorine substituents) bonded <u>trans</u> to chlorine. Crystal data for the carbene complex are: space group, $R\bar{3}$, a = 20.400(8) Å, α = 117.68°; ρ_{calcd} = 1.763 g cm^{-3}, ρ_{exptl} = 1.77 g cm^{-3}; Z = 6. This compound has Pt-L distances of: Pt-P = 2.220(2) Å,

Pt-Cℓ(1) = 2.347(3) Å, Pt-Cℓ(2) = 2.345(3) Å, Pt-C = 1.96(1) Å. The dihedral angle between the carbene and coordination planes is 84°. Certain preparations of the carbene complex exhibited two $\nu_{C=N}$ stretches in the infrared spectrum. X-ray crystallographic analysis of this crystal morphology indicated two crystallographically independent molecules which differ by approximately 20° in the dihedral angle between the carbene and coordination planes (84° versus 65°).

Bis(cyclopentadienyl) vanadium reacts with $[C_6H_5CNCH_3]BF_4$ to produce $[Cp_2V(C_6H_5CNCH_3)]BF_4$, which is the first complex prepared by direct reaction of a nitrilium salt with an organometal reagent. The complex has been shown by a X-ray crystallographic study to contain the nitrilium ion bound in dihapto fashion. The complex reacts with one equivalent of N-methyl-benzonitrilium tetrafluoroborate in CH_3CN to yield an as yet uncharacterized orange-brown material, but when reacted with two or three equivalents of $[C_6H_5CNCH_3]BF_4$ per complex $[Cp_2V(CH_3CN)_2](BF_4)_2$ results, in yields dependent on the stoichiometries of the reactants. The same orange-brown material also results.

ABSTRACT

SOME ORGANOMETALLIC CHEMISTRY OF IMINIUM SALTS

Dennis J. Sepelak, Ph. D.
Department of Chemistry
University of Illinois at Urbana-Champaign, 1981

The objective of this work was to investigate the reactions of iminium salts with various low-valent metal complexes in order to establish the possible modes of bonding and reactivity of the iminium moiety in organometallic compounds. Reactions of iminium salts, principally methylene iminium salts, with sodium cyclopentadienylirondicarbonyl, with tetrakis(triphenylphosphine)platinum(0), and several nickel(0) compounds are described.

Addition of sodium cyclopentadienylirondicarbonyl to $[CH_2{=}N(CH_3)_2]Cl$ at low temperatures yields $(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]$. Reactions of this compound are described, including photolytic decarbonylation to $(\eta^5\text{-}C_5H_5)Fe(CO)[\eta^2\text{-}CH_2N(CH_3)_2]$, in which the iminium moiety acts as an allyl-type donor to the metal. The infrared spectra of the series of complexes $(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2NR_2]$, $R_2=(CH_3)_2$, $(CH_2CH_2)_2CH_2$, $(CH_2CH_2)_2O$, $(CH_3)(C_6H_5)$, and $[CH_2CH(CH_3)_2]_2$, suggest there are equilibrium forms of the complexes in which there is interaction of the amino group of the iminium moiety with the iron center.

Reaction of bis(triphenylphosphine)nickel(ethylene) or tetrakis(triphenylphosphine)nickel(0) with methylene iminium salts gives $(Ph_3P)Ni(\eta^2\text{-}$

$CH_2NR_2)X$ from $[CH_2{=}NR_2]X$ and $\{(Ph_3P)_2Ni[\eta^2\text{-}CH_2N(CH_3)_2]\}ClO_4$ from $[CH_2{=}N(CH_3)_2]ClO_4$. Various physical measurements indicate these compounds are monomeric in solution and in the solid state, with a trigonally coordinated nickel. Addition of sodium cyclopentadienide to $(Ph_3P)Ni[\eta^2\text{-}CH_2N(CH_3)_2]Cl$ gives $(\eta^5\text{-}C_5H_5)Ni(PPh_3)[\eta^1\text{-}CH_2N(CH_3)_2]$.

Iminium salts, $[CH_2{=}NR_2]X$, X = halide, react with bis(1,5-cyclooctadiene)nickel(0) to form insoluble red complexes of stoichiometry $[CH_2NR_2]_2NiX_2$ in which the nickel is still zerovalent. Heating these complexes or their dissolution into polar solvents results in their transformation to blue complexes which are the corresponding substituted-ethylenediaminenickel(II) complexes, $(R_2NCH_2CH_2NR_2)NiX_2$. A similar coupling reaction of methylene iminium salts by nickel carbonyl in acetonitrile also produces ethylenediamines.

Heating of a mixture of $[CH_2{=}N(CH_3)_2]X$, X = Cl, Br, or I, and nickel carbonyl in tetrahydrofuran at 65°C produces $[\eta^2\text{-}CH_2N(CH_3)_2]Ni(CO)X$ in good yield. This reaction is similar to the known reaction of allyl halides with nickel carbonyl, which produces allyl-nickel halide dimers, apparently through an allyl-nickel(carbonyl) halide intermediate. The complexes $[\eta^2\text{-}CH_2N(CH_3)_2]Ni(CO)X$ undergo reaction with various electrophiles to form organonitrogen compounds. These nickel complexes may have a utility in organic synthesis similar to that of allyl-nickel halide dimers.

When tetrakis(triphenylphosphine)platinum(0) is stirred with $[CH_2{=}N(CH_3)_2]Cl$, a complex of stoichiometry $(Ph_3P)Pt[CH_2N(CH_3)_2]_2Cl_2$ is isolated. This complex contains a metallocycle ring $\overline{PtCH_2N(CH_3)_2CH_2N}(CH_3)_2$, apparently formed via nucleophilic attack of the amino group of a $PtCH_2N(CH_3)_2$ moiety on a second iminium ion, followed by cyclization.

The iron, nickel, and platinum complexes obtained demonstrate that several different modes of bonding are possible for the iminium moiety in organometallic compounds. Iron complexes were isolated in which the iminium moiety is η^1-bound, acting as an σ-donor, or η^2-bound, acting as an allyl-type donor ligand. In the various nickel complexes the iminium moiety is attached as an η^2-ligand whose bonding can be considered to be either a π-bond like an olefin, or alternatively as an allyl-type bonding to the metal. Finally, the isolation of the platinum complex described above demonstrates that a metallocycle ring of two iminium moieties can be formed.

Organometallic Chemistry of Carbon–Nitrogen Multiple Bonds. 2. Reactions of Cyclopentadienyldicarbonyliron Anion with Iminium Salts; Chemistry of the Products

E. Kent Barefield* and D. J. Sepelak

Contribution from the School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332. *Received November 3, 1978*

Abstract: Reactions of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ with $[R_2C{=}NR'_2]X$ produce dialkylaminoalkyl complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CR_2NR'_2)]$ except when R is a primary or secondary alkyl group; in these cases an enamine and $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ are formed by an acid–base reaction. Unusual infrared and NMR spectra exhibited by a series of complexes of the type $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2NR_2)]$ are interpreted as a result of detection of rotational isomers (about the Fe–CH_2 bond) in which there is an intramolecular iron–nitrogen interaction. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]]$ reacts, at nitrogen, with electrophiles; HCl and CH_3I give salts, which may be considered as derivatives of the nitrogen ylides $^-CH_2N^+(CH_3)_2H$ and $^-CH_2N^+(CH_3)_3$, whereas BF_3 and BH_3 give simple adducts. Reaction with CH_3COCl, $(CF_3CO)_2O$, or $(CF_3SO_2)_2O$ occurs with carbon–nitrogen bond cleavage to produce $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2Cl$, $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2O\text{-}COCF_3$, and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]N(CH_3)_2]O_3SF_3$, respectively. Photolysis of the $\eta^1\text{-}CH_2N(CH_3)_2$ derivative produces $[(\eta^5\text{-}C_5H_5)Fe(CO)[\eta^2\text{-}CH_2N(CH_3)_2]]$, which reacts with phosphines (L) to produce $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)[\eta^1\text{-}CH_2N(CH_3)_2]]$.

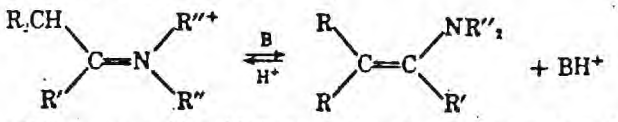
Introduction

As described in an earlier paper,[1] we have undertaken an investigation of the organometallic chemistry of a number of species containing carbon–nitrogen multiple bonds.[2] Our initial efforts have involved the preparation of complexes of iminium ions, $R_2C{=}NR'_2{}^+$. We have already described reactions of $(Ar_3P)_4Ni$ and $(Ar_3P)_2NiC_2H_4$ with $CH_2{=}NR_1R_2{}^+$, which yield products that contain the iminium ion bonded in a dihapto fashion.[2] One of these products, $[Ph_3PNi(Cl)[\eta^2\text{-}CH_2N(CH_3)_2]]$ was converted to $[(\eta^5\text{-}C_5H_5)Ni[\eta^1\text{-}CH_2N(CH_3)_2]PPh_3]$ by treatment with sodium cyclopentadienide. It seemed likely that complexes containing the iminium ion moiety bonded in monohapto form might be prepared directly by reaction of iminium salts with metal carbonyl anions since iminium ions are susceptible to nucleophilic attack at carbon.[3] Species containing the >C–N< moiety in a dihapto configuration might then be obtained by intramolecular substitution of a carbonyl ligand by the amino group. We chose cyclopentadienyldicarbonyliron anion as the first nucleophile for study because of its ready availability and known nucleophilic properties. This paper reports the results of our work on the reactions of this nucleophile with a variety of iminium salts and novel aspects of the physical characterization and chemistry of the products obtained. While our studies on this system were in progress, Wilkinson and Fong reported reactions of some other metal carbonyl anions with dimethylmethyleneiminium iodide.[4a] Other somewhat related compounds that contain dihapto bonded C–N moieties have also been reported.[4b]

Results and Discussion

A summary of the preparative chemistry to be discussed in the following sections is given in Figure 1. The Experimental Section should be consulted for details of the individual reactions.

Reactions of Iminium Salts with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$. Reactions of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ (hereafter $\eta^5\text{-}C_5H_5$ will be donated by Cp) with suspensions of iminium salts in THF occur rapidly, even at −78 °C, regardless of the extent of substitution of the iminium ion. The nature of the products obtained depends upon the type of substituent present in the iminium ion and to some extent upon the reaction temperature. Methylene iminium ions, $[CH_2{=}NR_2]^+$, invariably yield dark red complexes of the type $[CpFe(CO)_2(\eta^1\text{-}CH_2NR_2)]$ when reactions are conducted at −78 °C. Six complexes of this type were prepared (entries **1–6** in Table I). Information pertinent to their characterization is given in the following section. At room temperature only low yields of the aminoalkyl species are obtained; $[CpFe(CO)_2]_2$ is the principal iron containing product. The necessity of conducting these reactions at low temperature probably accounts for the failure of earlier workers to obtain the aminoalkyl product.[5] Likewise carbon-substituted iminium ions that do not have protons on the α carbon, such as $[(CH_3)_2C(CH_2C_6H_5)CH{=}N(CH_2CH_2)_2O]^+$, react at −78 °C to yield analogous products. However, C-substituted iminium salts that have one or more protons on the α carbon ultimately give $[CpFe(CO)_2]_2$ as the iron-containing product. The reaction of $[(CH_3)_2CHCH{=}N(CH_2CH_2)_2O]^+$ was studied in some detail. Salts of this ion reacted immediately with $CpFe(CO)_2{}^-$ at −78 °C to form a pale yellow solution. Upon warming to room temperature the solution darkened to the color of $[CpFe(CO)_2]_2$, which was subsequently isolated from the reaction mixture. In separate experiments enamine, $(CH_3)_2C{=}CHN(CH_2CH_2)_2O$, and $CpFe(CO)_2H$ were detected by NMR as products of the initial reaction. The interconversion of iminium ions and enamines by acid–base reactions, i.e.



is well documented[3] and it is likely that simple proton transfer to the carbonyl anion leads to the products observed. Although its pK value has not been determined, the carbonyl anion apparently behaves as a base in other reactions. For example, a standard preparation of $CpFe(CO)_2H$ involves the reaction of the carbonyl anion with *tert*-butyl chloride.[6] Although this is sometimes cited as an example of a β-hydride elimination reaction,[7] implying that nucleophilic displacement of chloride and formation of the alkyl compound precede the decomposition, recent work shows that $CpFe(CO)_2C(CH_3)_3$ prepared by an alternative route is quite stable.[8] The most likely pathway for hydride production is dehydrohalogenation (E2 elimination). In fact, Reger's work on the decomposition of $CpFe(CO)(PPh_3)CH_2CH_2R$, which does occur by a β-elimination process, shows that ligand dissociation is required prior

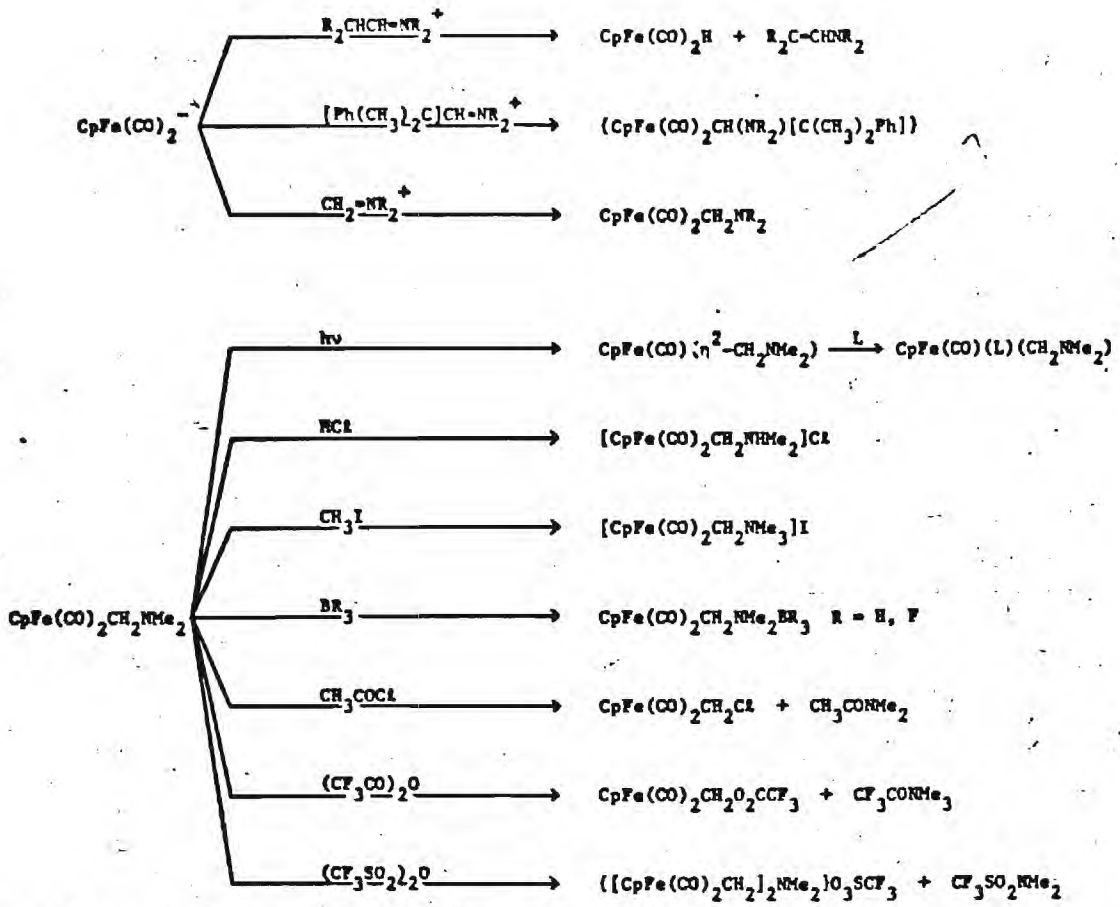


Figure 1. Summary of preparative chemistry involving $CpFe(CO)_2^-$ and iminium salts.

to the hydride transfer step.[9] Since thermal loss of CO is negligibly slow at room temperature in the $CpFe(CO)_2CH_2NR_2$ compounds, the β-hydride pathway can be eliminated as a possibility in the C-substituted iminium ion reactions.

The previously mentioned reduced yields of the aminoalkyl complexes obtained from reactions that were conducted at room temperature is puzzling since the aminoalkyl complexes are not especially thermally sensitive. It seems more likely that an alternative pathway for reaction, such as electron transfer, may compete with the nucleophilic path at the higher temperature. Production of 17 electron $CpFe(CO)_2$ would result in dimer formation and presumably $R_2NCH_2CH_2NR_2$ (or R_2NCH_3 depending upon the fate of the aminoalkyl radical). Both nucleophilic and electron transfer pathways have been suggested for reactions of organometallic anions with certain alkyl halides.[10] The effect of temperature on these reactions is not readily predicted but it should be noted that the nature of the carbonyl reagent is probably different at high and low temperatures since the ratio of solvent separated to contact ion pairs should be substantially different.[11] Whether or not this could affect the redox and/or nucleophilic properties of the anion remains to be determined.

All of the aminoalkyl complexes studied are viscous red oils that are air sensitive but are only moderately thermally sensitive. In fact, the lower molecular weight derivatives can be distilled at 50 °C in vacuo with little decomposition, although they do decompose when heated at higher temperatures. $[CpFe(CO)_2]_2$ forms in the thermal decomposition. Higher molecular weight derivatives are not distillable and could not be obtained in analytically pure form as the free amines. All of the aminoalkyl compounds could be obtained as crystallizable solids by complexation with Lewis bases, vide infra.

Several unsuccessful attempts were made to generate aminoalkyl complexes by other routes. $CpFe(CO)_2CH_2Cl$ was unreactive toward $LiN(C_2H_5)_2$, a result that is not surprising in view of the similarity of this complex to neopentyl systems. Green et al. found that the chloromethyl complex reacted with silver ion and on the basis of the product distribution suggested that unstable $[CpFe(CO)_2CH_2]^+$ was formed.[12] It seems reasonable that such a species would react readily with dialkylamines. Unfortunately, no conditions were found where Ag^+ would react with the chloromethyl complex in the presence of diethylamine.

IR and NMR Spectra of $[CpFe(CO)_2(\eta^1\text{-}CH_2NR_2)]$. As many as six carbonyl stretching absorptions are observed for $[CpFe(CO)_2(\eta^1\text{-}CH_2NR_2)]$ depending upon the nature of the substituents on nitrogen; the energies of certain of these absorptions are lower than expected for compounds with such alkyl substituents,[13] vide infra. In addition the NMR chemical shifts of the methylene group proton resonances are anomalously low for those complexes having low frequency infrared absorptions.

Carbonyl region infrared spectra of five derivatives are shown in Figure 2 (**6** has a spectrum identical with that of **4**). These five compounds can be classified into three categories based on their infrared spectral behavior: (a) **1**; ν_{CO} expected for an aminomethyl substituent, one pair of absorptions observed; (b) **5**; ν_{CO} at lower energy than expected, two pairs of absorptions observed;[14] (c) **2–4**; ν_{CO} at expected frequencies, one pair, and ν_{CO} at lower energy, two pairs, with relative intensities of high and low energy pairs of bands varying with the substituents on nitrogen. Infrared spectra of **3** obtained at several temperatures between +30 and −50 °C show that the intensities of the lower energy pairs of absorptions increase relative to those of the high energy pair as the temperature is lowered.

Room temperature NMR spectra of all of the aminoalkyl complexes (chemical shift data are tabulated in the table) are

to their complexes. Derivatization of substituted alkyl complexes could develop into a general method for generating ylide complexes, especially of those ylides that are inherently unstable. We earlier reported the preparation of $[CpNi(PPh_3)CH_2N(CH_3)_3]I$ by methylation of the aminoalkyl complex[1] and we have prepared the sulfur ylide complex, $[CpFe(CO)_2CH_2S(CH_3)CH_2CH_3]I$ by reaction of the thioether with $[(CH_3)_3O]BF_4$. Similar alkylations of $RSCH_2ML_n$ species have been performed by others.[27]

In view of the above results it is not surprising that the aminoalkyl complexes also react readily with Lewis acids. Both BF_3, **9**, and BH_3, **10**, complexes of $\{CpFe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]\}$ were prepared. These yellow complexes resemble closely the ylide complexes in their spectroscopic properties (Table I). Both show shifts of their carbonyl stretching absorptions to higher energy compared with the parent. The spectra are simplified (two bands for each adduct) for the same reasons described for the quaternary derivatives. The methylene group chemical shifts are at *higher field* than that of the dimethylaminomethyl complex, although the chemical shifts of cyclopentadienyl and methyl proton resonances are somewhat less affected than in the quaternary derivatives.

Low-temperature reaction of $\{CpFe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]\}$ with CH_3COCl, $[CF_3CO]_2O$, or $[CF_3SO_2]_2O$ results in cleavage of the methylene carbon–nitrogen bond. Products of these reactions are $CpFe(CO)_2CH_2Cl$, $CpFe(CO)_2CH_2OC(O)CF_3$ (**11**), and $\{[CpFe(CO)_2CH_2]_2N(CH_3)_2\}O_3SCF_3$ (**12**), respectively, and the appropriate dimethylamides. The first two reactions probably proceed in the following fashion:

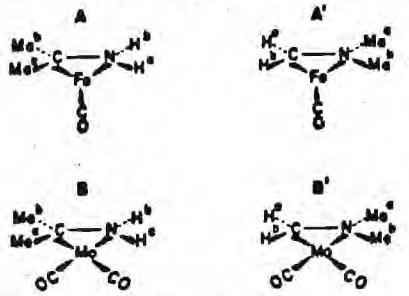
$$CpFe(CO)_2CH_2N\!<\!\!\begin{matrix}\\ \\ \end{matrix} + RCX \rightleftharpoons CpFe(CO)_2CH_2\overset{O}{\overset{\|}{N}}CR^+ + X^-$$

$$CpFe(CO)_2CH_2\overset{O}{\overset{\|}{N}}CR^+ + X^- \longrightarrow CpFe(CO)_2CH_2X + RCN\!<\!\!\begin{matrix}\\ \\ \end{matrix}$$

Whether the second step proceeds by S_N2 displacement of the amide by the counterion or a dissociative (S_N1) reaction is not known. Other work suggests that the carbenoid species $[CpFe(CO)_2CH_2]^+$ is not stable[29] so that a purely dissociative reaction either does not occur or occurs in a tight ion pair where the counterion traps the carbene species before disproportionation takes place. The ultimate disproportionation products should be $[CpFe(CO)_2(C_2H_4)]X$ and/or $CpFe(CO)_2X$. Neither of these was observed.

The reaction with $(CF_3SO_2)_2O$ probably proceeds through an ionic intermediate analogous to that above but excess $CpFe(CO)_2CH_2N(CH_3)_2$ (the anhydride was added to the aminomethyliron complex) either reacts with the ionic species or with the trifluorosulfonate which could form as an intermediate product. The dinuclear product is similar to products derived from the deprotonated phosphorus ylide $[(CH_3)_2P(CH_2)_2]^-$.[30]

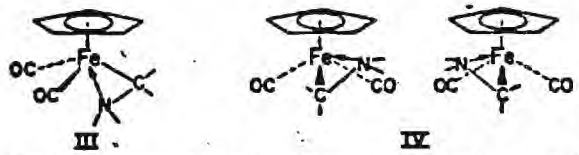
Preparation and Reactions of $\{CpFe(CO)[\eta^2\text{-}CH_2N(CH_3)_2]\}$. Photolysis of $\{CpFe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]\}$ results in smooth evolution of CO with the formation of the η^2-iminium ion complex **13**, a low melting solid which is readily sublimed in vacuo. As expected this complex shows a single carbonyl stretching absorption (1903 cm^{-1} in cyclohexane). Its NMR spectrum (Table I) consists of a singlet for the cyclopentadienyl protons and *doublets* for the methylene and methyl group protons. As shown by A below, a fixed orientation of the dihapto iminium ion would result in nonequivalent methylene protons and methyl groups. The NMR spectrum confirms this structure and indicates that interconversion between A and A′ is slow at room temperature. In fact, the NMR spectrum is unchanged to ~100 °C (toluene solution) where the complex begins to decompose. This behavior is in contrast to that described by Wilkinson and Fong for $\{CpMo(CO)_2[\eta^2\text{-}CH_2N(CH_3)_2]\}$.[4a] The room temperature ^1H NMR spectrum of this complex consists of three singlets at τ 4.64, 7.31, 7.48 in the ratio 5:6:2, respectively. As shown by structure B, this



complex should also have nonequivalent methylene protons and methyl groups and the observed NMR spectrum suggests that the complex is undergoing a rapid intramolecular rearrangement (B ↔ B′). We have confirmed that this is the case through variable temperature NMR measurements on $CDCl_3$ solutions of the complex. The two higher field resonances broaden as the temperature is lowered so that at −60 °C two doublets are clearly present consistent with static structures B and B′. The different behavior of the iron and molybdenum complexes of the η^2-$CH_2N(CH_3)_2$ ligand resembles that of the corresponding η^3-allyl complexes. $CpFe(CO)_2$(allyl) complexes rearrange (endo → exo) at moderate rates at room temperature. $\Delta G^{\ddagger}$ is 24.1 kcal/mol for the methallyl complex.[31] The comparable rate of conversion of anti ↔ syn groups to endo ↔ exo isomerization suggests that an η^3–η^1–η^3 process is responsible. In contrast, $CpMo(CO)_2$(allyl) complexes undergo rapid interconversion (endo ↔ exo) at room temperature with static forms observed (by ^1H NMR) at temperatures below 0 °C. $\Delta G^{\ddagger}$ for the intramolecular process in the methallyl complex is about 16 kcal/mol.[32] Anti–syn interconversion does not accompany the endo ↔ exo process leading to the conclusion that ". . . a rotation of the planar allyl about an axis between the metal and the center of gravity of the allyl appears most reasonable".[32] Although activation parameters and mechanistic details are not presently available for the iminium ion complexes, it is apparent that the relative stereochemical rigidities of iron and molybdenum compounds are the same as that of the allyl complexes. This observation suggests that the similarity between the η^3-allyl and η^2-iminium ligands is more than operational; they seem to impart much the same electronic effect to the metal.

$\{CpFe(CO)[\eta^2\text{-}CH_2N(CH_3)_2]\}$ undergoes facile ring opening reactions with phosphines as evidenced by NMR and infrared spectra of reaction mixtures containing $PhP(CH_3)_2$ and Ph_2PCH_3. The monophosphine complexes $\{CpFe(CO)L[\eta^1\text{-}CH_2N(CH_3)_2]\}$, **14** and **15**, are asymmetric and their NMR spectra (Table I) contain multiplets consistent with the diasterotopic nature of the methylene protons and the methyl groups in the $PhP(CH_3)_2$ compound. Infrared spectra of the phosphine complexes contain a single symmetrical carbonyl stretching absorption (see Table I). The absence of any complexity to these spectra indicates that only one rotational isomer is present or, perhaps more likely, that the carbonyl stretching absorptions of the rotational isomers present (three are possible) are not sufficiently different in energy to be resolved and are contained in the absorption envelope. (The half-widths of the carbonyl bands are ~20 cm^{-1}, which is about twice the half-width of absorptions for the $CpFe(CO)_2(\eta^1\text{-}CH_2NR_2)$ derivatives.) Neither of the phosphine complexes could be crystallized; however, complexation of the amino nitrogen in

The infrared and NMR spectral data are only consistent with the existence of a dynamic equilibrium between isomeric species in the case of **2–6**, whereas only a single species is detectable for **1**. At least three species are required for **2–4** and **6** and two of these, as well as the two detected for **5**,[14] have lower energy carbonyl infrared stretching absorptions than expected for such alkyl substituents. The low CO stretching frequencies and the existence of two similar species with low energy absorptions can be accounted for by species III and IV:



III IV

in which there exits a net bonding interaction between the nitrogen atom and iron.[22] The increased electron density placed on iron as a result of this perturbation is transferred (in part) to the π^* orbitals of CO through the normal back-bonding interaction (which occurs here via the iron d_{xy}, $d_{x^2-y^2}$, and d_{z^2} orbitals)[25] resulting in a decrease in the C–O bond order and a reduction of the C–O stretching energy. Structures III and IV represent the same rotational isomers as I and II *with* the addition of the Fe–N interaction. The additional set of absorptions (highest energy peak) observed for **2–4** and **6** and the only set observed for **1** are in the energy range expected for such alkyls. We attribute these to a form in which there is no Fe–N interaction. In principle, rotational isomers exist for this species but their carbonyl absorptions are apparently not sufficiently different in energy to be resolved.

Consistent with the above interpretation, the increase in the ratio of interacting to noninteracting forms in going from **1** to **5** roughly parallels the increase in basicity of the secondary amine from which they are formally derived. The temperature dependence of the equilibrium is in the expected direction and the small enthalpy difference is consistent with the weak nature of the Fe–N interaction. The effect of complexation of the nitrogen by an external acid is also to be expected.

The chemical shifts observed for the methylene groups in **1–6** are obviously a mole fraction weighted average of the species participating in each equilibrium; the shifts of **1** and **5** should be close to the limits for noninteracting and interacting forms, respectively. The pronounced deshielding effect resulting from the Fe–N interaction is not readily explained. It does not seem reasonable that the inductive effect resulting from the interaction should be greater than that of a proton or methyl carbonium ion. Perhaps the precise location of the methylene protons relative to other parts of the molecule in the interacting form results in a deshielding effect.

Reactions of $[CpFe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]]$ with Electrophiles. The aminoalkyl complexes react, at nitrogen, with a variety of electrophilic reagents including Brønsted acids, alkyl halides, Lewis acids, carboxylic and sulfonic acid halides, and anhydrides. Although it is probably safe to assume that these reagents react with the aminoalkyl compounds, regardless of the identity of the nitrogen substituents, not all combinations have been attempted and only reactions with the more extensively studied dimethylaminomethyl complex **4** will be described.

Complex **4** reacts immediately in petroleum ether with $HCl_{(g)}$ or CH_3I to give yellow precipitates (**7** and **8**, respectively). Both products are recrystallizable from polar solvents without change. Elemental analysis, IR, and ^1H NMR data are consistent with the formulation of these products as $[CpFe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2R]]X$: **7**, R = H, X = Cl; **8**, R = CH_3, X = I. The effects of introducing a strongly electron-withdrawing group into the molecule are readily apparent in the infrared and NMR spectra. In the former, the carbonyl

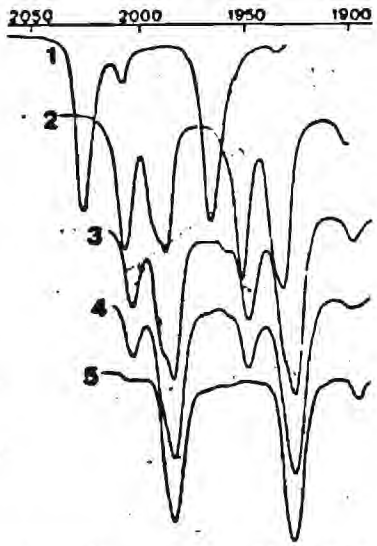


Figure 2. Carbonyl stretching absorptions of $[CpFe(CO)_2(\eta^1\text{-}CH_2NR_2)]$ (cyclohexane solutions): NR_2 = (1) $N(CH_3)Ph$, (2) $N(CH_2CH_2)_2O$, (3) $N(CH_2CH_2)_2CH_2$, (4) $N(CH_3)_2$, (5) $N[CH_2CH(CH_3)_2]_2$. Absorptions at ~1900 cm^{-1} in spectra **2–5** are due to $[CpFe(CO)(\eta^2\text{-}CH_2NR_2)]$ impurities. The absorption at 2007 cm^{-1} in **1** is from $[CpFe(CO)_2]_2$.

stretching absorptions are shifted to higher energy compared with the parent molecule (Table I gives spectral data) consistent with electron density withdrawal from the metal and concomitant reduction in Fe–CO π-backbonding. Only two CO stretching absorptions are observed in both cases, rather than the six observed for the parent. Simpler spectra should be observed since the Fe–N interaction that results in stabilization of rotational isomers in the parent is blocked in the derivatives. Rotational isomers of the normal type are still possible but are not detected in the infrared spectra. The NMR spectra show downfield shifts of the cyclopentadienyl and methyl group resonances consistent with the deshielding that results from introduction of the positive charge. The methylene group resonances occur *upfield* of those in the parent. A satisfactory explanation for this phenomenon is not available but it must be associated with the unusual properties of the dimethylaminomethyl complex and not those of the quaternized forms. In fact, if the chemical shift of the methylphenylaminomethyl complex **1**, which shows "normal" behavior, is chosen as the reference (τ 7.43), then the shifts of both the protonated and methylated complexes are downfield (τ 6.71 and 6.0, respectively) as would normally be expected.

The quaternary salts are extremely resistant to hydrolysis, even in strong aqueous acid and they are unaffected by trifluoroacetic acid. Treatment of the protonated complex with K_2CO_3 in acetonitrile regenerates the starting material. The salts are also resistant to air oxidation both in solution and in the solid state.

$[CpFe(CO)_2CH_2N(CH_3)_3]^+$ and $[CpFe(CO)_2CH_2NH(CH_3)_2]^+$ may be considered as substitution products derived from reactions of $[CpFe(CO)_2L]^+$ with the ylides $^-CH_2N^+(CH_3)_3$ and $^-CH_2N^+(CH_3)_2H$, respectively. In fact, the related phosphorus derivative, $[CpFe(CO)_2CH_2PPh_3]BF_4$, has been prepared by reaction of $[CpFe(CO)_2(THF)]BF_4$[26a] or $CpFe(CO)_2I$,[26b] in the presence of $AgBF_4$, with the preformed ylide, $^-CH_2P^+Ph_3$. In contrast to phosphorus, simple nitrogen ylides are not isolable and can apparently only be generated as LiBr stabilized species.[27] Although a fair amount of organic chemistry has been done with these LiBr complexed species, transition metal complexes have not been generated from them. Of course, neither $^-CH_2N^+(CH_3)_2H$ nor $^-CH_2P^+(CH_3)_2H$ can be generated in the usual fashion from the quaternary salt so that protonation of substituted alkyl complexes represents a unique route

Table I. Infrared and ^1H NMR Spectral Data for $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2NR_2$ and Derivatives

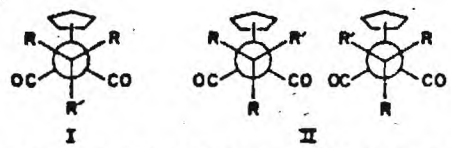
compound	IR[a]		NMR[b]		
			$\eta^5\text{-}C_5H_5$	Fe-CH_2	other
1 $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(C_6H_5)CH_3]]$	2026	1966	5.65[c]	7.43	NCH_3, 7.30, $-C_6H_5$, cm centered at τ 3.15
2 $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_2CH_2)_2O]]$	2008 1993 sh 1988	1952 1937 sh 1933	5.75[c]	6.13	NCH_2CH_2O, 6.42 ct; NCH_2CH_2O, 7.72 ct
3 $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_2CH_2)_2CH_2]]$	2003 1991 sh 1985	1949 1933 sh 1927	5.73[c]	5.78	NCH_2, 7.63 cm; $-(CH_2)_3-$, 8.52 cm
4 $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]]$	2007 1992 sh 1987	1952 1935 sh 1930	5.76[c] 5.26[d] 5.40[e]	5.76 5.69 5.77	7.90 7.89 7.90
5 $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_2CH(CH_3)_2)_2]]$	1991 sh 1987	1930	5.77[c]	5.60	NCH_2CH, 7.83 cm; NCH_2CH, 8.32 cm; $CH(CH_3)_2$, 9.08 d, J = 6 Hz
6 $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)CH_2CH_3]]$	2005 1991 sh 1887	1950 1930	5.85[c]	5.69	NCH_3, 7.87, $-CH_2CH_3$, 7.71 q; $-CH_2CH_3$, 8.01 t, J = 7 Hz
7 $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2NH(CH_3)_2]]Cl$	2027	1969[d]	4.73[d]	6.71	7.30
8 $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_3]]I$	2031	1972[d]	4.79[d]	6.00	6.93
9 $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2(BH_3)]]$	2016	1963[d]	5.80[c]	6.43	7.58
10 $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2(BF_3)]]$	2022	1962[d]	6.02[c]	6.50	7.78
11 $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2OC(O)CF_3]]$	2032	1980	5.88[c]	4.63	
12 $[[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2)]_2N(CH_3)_2]O_3SCF_3$	2025	1970	4.83[d]	6.07	7.20
13 $[(\eta^5\text{-}C_5H_5)Fe(CO)[\eta^2\text{-}CH_2N(CH_3)_2]]$		1903	5.74[c] 5.61[d]	7.39, 8.02 7.15, 8.03	8.16, 8.21 7.63, 7.83
14 $[(\eta^5\text{-}C_5H_5)Fe(CO)[P(C_6H_5)(CH_3)_2][\eta^1\text{-}CH_2N(CH_3)_2]]$		1912	5.86[c] J_P = 1.5 Hz	6.49 d, 6.57 d J_P = 3.2 Hz	NCH_3, 7.67, PCH_3; 8.71 d, 8.79 d, J_P = 3.9 Hz; PC_6H_5, 2.55–2.97 cm
15 $[(\eta^5\text{-}C_5H_5)Fe(CO)[P(C_6H_5)_2CH_3][\eta^1\text{-}CH_2N(CH_3)_2]]$		1914	5.72[c] J_P = 2 Hz	6.33 d, 6.45 d J_P = 3 Hz	NCH_3, 7.72, PCH_3, 8.42 d, J_P = 8 Hz; PC_6H_5, 2.33–3.03 cm

[a] Spectra were taken on cyclohexane solutions unless otherwise indicated. Conditions are described in the Experimental Section. [b] Chemical shifts are τ values vs. Me_4Si as internal standard. Solvents are indicated by appropriate footnote letter. Abbreviations used to describe multiline patterns are: d, doublet; t, triplet; q, quartet; ct, complex triplet; cm, complex multiplet. [c] Benzene-d_6. [d] Acetonitrile-d_3 for NMR, acetonitrile for IR. [e] Carbon disulfide.

entirely consistent with their formulation and all contain only one resonance assignable to the methylene group; it is a singlet in each case. The spectrum of 4 was examined (as a toluene-d_8 solution) at −80 °C; again the methylene resonance consisted of one singlet. The chemical shifts of the methylene group singlets are anomalously low for compounds 2–6, which also have unusual infrared spectra, whereas the shift of the resonance for 1 is as predicted.[15] The chemical shift of the methylene resonance increases as the relative intensity of the low frequency pairs of infrared bands increases.

Methylation, protonation, or adduct formation reactions of 4 yield compounds whose infrared spectra contain only one pair of carbonyl stretching absorptions vide infra. In each case, these occur at the higher frequencies expected for compounds with such electron-withdrawing substituents. The NMR chemical shifts of the methylene group proton resonances (singlets in each case) are *upfield of that of the parent compound.*

In general, complexes of the type $(Cp)Fe(CO)_2R$ exhibit two or more carbonyl stretching absorptions depending upon the symmetry and size of R and the frequencies of the absorptions increase as the electron-withdrawing power of R becomes greater.[15] More than two carbonyl absorptions *may be* observed when R has lower than threefold symmetry. For example, when R has only a plane of symmetry, two rotational isomers exist as a result of restricted rotation about the bond to iron, i.e.



When the energies of the carbonyl stretching absorptions for these isomers are sufficiently different so that they can be resolved, four bands (two pairs) are observed.[16-21] This is the case when R is $SiHCl_2$,[16-18] $GeHCl_2$,[19] and CH_2Ph.[20]

$[CpFe(CO)(PPh_2CH_3)[\eta^1\text{-}CH_2N(CH_3)_2]]$ by BF_3 produced a solid derivative **16** whose elemental analysis and spectroscopic properties are consistent with the desired compound and confirm the authenticity of the precursor complex.

Conclusion

This work and that of Wilkinson[4a] show that, subject to a few constraints, aminoalkyl complexes are readily obtained from reactions of iminium salts and metal carbonyl anions. The aminoalkyliron products undergo a number of reactions to produce novel compounds not readily available by other routes. Several of these reactions should be applicable to aminoalkyl complexes of most metals. Of special interest is C–N bond cleavage by electrophilic reagents which may provide a route to carbene complexes that do not have heteroatom substituents. Work in this area is underway.

The iron–nitrogen interaction proposed to occur in $CpFe(CO)_2(\eta^1\text{-}CH_2NR_2)$ species on the basis of infrared and NMR measurements is unusual and more definitive evidence would be desirable. Unfortunately, all of the compounds believed to have this interaction are liquids at ambient temperature so that X-ray data are not obtainable with our equipment. Neither of the phosphine complexes appear to have iron–nitrogen interactions. This could be because of unfavorable steric effects or because of the decrease in π-bonding capability of the phosphorus donor.

Experimental Section

All synthetic operations and manipulations of samples of organometallics were conducted in a nitrogen filled glovebox or under a nitrogen atmosphere in suitable glassware by using syringe techniques for sample transfer. Solvents were purified by distillation from drying agents under a nitrogen atmosphere. Iminium salts were prepared by literature methods and each was characterized by its NMR spectral properties and by elemental analysis before use.

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]]$, 4. A solution of $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$, 75 mmol obtained by stirring 13.35 g of $[Fe(CO)_2(C_5H_5)]_2$ with an excess of 1% sodium amalgam in THF for several hours and decanted into a dropping funnel, was added over 1 h to 7.50 g (80 mmol) of $[(CH_3)_2NCH_2]Cl$ suspended in 75 mL of THF at −78 °C. After stirring for an additional 1.5 h at −78 °C, the reaction mixture was warmed to room temperature and the solvent evaporated. The residue was extracted four times with 35-mL portions of medium petroleum ether. After the extracts were filtered through a pad of Celite, the solvent was evaporated to yield 14.8 g (84%) of a dark, air-sensitive red-brown oil. Subsequent distillation in a molecular still at 50–55 °C (10^{-3} mm) gave pure $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[CH_2N(CH_3)_2]]$. Anal. Calcd for $C_{10}H_{13}NFeO_2$: C, 51.10; H, 5.57; N, 5.96; Fe, 23.76. Found: C, 51.00; H, 5.40; N, 6.00; Fe, 23.26.

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)C_6H_5]]$, 1. A solution of 13 mmol of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ in 40 mL of THF, prepared as described above, was added to a suspension of 2.0 g (13 mmol) of $[CH_2N(CH_3)C_6H_5]Cl$ in 100 mL of THF at −78 °C over a 45-min period. After stirring at −78 °C for an additional 2 h, the reaction mixture was gradually warmed to room temperature and the solvent evaporated. The residue was extracted four times with a 1:1 mixture of hexane/ether. The extracts were filtered through Celite, combined, and the solvent evaporated to yield 2.7 g (70%) of a red-brown oil. Chromatography of the product on silica gel, alumina, or charcoal/Celite resulted in decomposition. However, chromatography on a column of Celite with hexane yielded the product as a dark orange-red oil, contaminated with only a small amount of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2$ (by infrared spectroscopy). The compound decomposes extensively to $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and a colorless oil upon standing at 0 °C over a week.

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_2CH_2)_2O]]$, 2. A solution of 20 mmol of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ in 40 mL of THF was added over 45 min to a suspension of 3.0 g (22 mmol) of $[CH_2N(CH_2CH_2)_2O]Cl$ in 85 mL of THF at −78 °C. After stirring an additional hour at −78 °C, the reaction flask was allowed to warm slowly to room temperature. Workup as described for **4** (extracted six times with a total of 100 mL of hexane) gave 5.2 g (94%) of the product as a dark red oil. Satisfactory analytical results for all elements could not be obtained on individual samples of **2** or **3**. However, their NMR spectra (Table I) were entirely consistent with their proposed structures and their infrared spectra did not vary with the particular preparation.

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_2CH_2)_2CH_2]]$, 3. A solution of 25 mmol of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ in 50 mL of THF was added to a suspension of 4.0 g (30 mmol) of $[CH_2N(CH_2CH_2)_2CH_2]Cl$ in 75 mL of THF at −78 °C over a 1-h period. Workup of the reaction mixture as described above gave 5.3 g (77%) of the product as a red-brown oil. Distillation as above gave the product.

$(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N[CH_2CH(CH_3)_2]_2]$, 5. A solution of 20 mmol of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ in 40 mL of THF was added slowly to a suspension of 3.75 g (21 mmol) of $[CH_2N(CH_2CH(CH_3)_2)_2Cl$ in 75 mL of THF at −78 °C. Workup as above gave 5.2 g (82%) of the desired product. Distillation in high vacuum at 50 °C in a molecular still apparatus gave the product. Anal. Calcd for $C_{16}H_{25}FeNO_2$: C, 60.18; H, 7.90; N, 4.39. Found: C, 60.63; H, 8.43; N, 4.92.

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)(CH_2CH_3)]]$, 6. Reaction of 10 mmol of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ and 1.1 g (10 mmol) of $[CH_2N(CH_3)(CH_2CH_3)]Cl$ and workup as above gave 1.1 g (44%) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[CH_2N(CH_3)(CH_2CH_3)]]$. Anal. Calcd for $C_{11}H_{15}NFeO_2$: C, 53.04; H, 6.07; N, 5.62; Fe, 22.42. Found: C, 53.32; H, 6.04; N, 5.65; Fe, 21.22.

Reaction of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ with $[(CH_3)_2CHCH{=}N(CH_2CH_2)_2O]Cl$. A solution of 4.5 mmol of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ in 30 mL of THF was added dropwise over ca. 30 min to a suspension of 0.8 g (4.5 mmol) of the iminium salt in THF, which was maintained at −78 °C during the entire addition. Decolorization of the dark red-brown color of the carbonyl anion was rapid as each drop entered the iminium ion suspension. A pale yellow color persisted. After addition was complete the mixture was allowed to warm to room temperature with continuous stirring. After this time the mixture was a dark red-brown color. The solvent was removed under vacuum and the residue was extracted with 20 mL of pentane. After filtration the pentane was evaporated to leave a red-brown oily residue. An NMR spectrum obtained on this residue showed strong resonances for the enamine $(CH_3)_2C{=}CHN(CH_2CH_2)_2O$. In addition to resonances for the enamine, there were resonances attributable to the protons of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ as well as some unassigned resonances. The enamine constituted at least 60% of the sample.

In a second experiment, a solution of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ (prepared from 0.89 g (2.5 mmol) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and excess Na(Hg) in about 10 mL of THF) was slowly added to a cooled (−96 °C toluene slush) flask that contained 0.90 g (5.0 mmol) of $[(CH_3)_2CHCH{=}N(CH_2CH_2)_2O]Cl$. The reactants were mixed by swirling and allowed to warm slightly by removal of the flask from the bath for short periods. The iminium salt gradually disappeared over about 30 min after which time a portion of solution was filtered into a cold NMR tube. A small quantity of toluene was added to the tube as a standard. The presence of a hydride was established by a singlet 18-ppm upfield from the phenyl proton resonance of toluene. A cyclopentadienyl proton resonance approximately five times as intense as the hydride resonance was also present and was assumed to be due to $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$.

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2NH(CH_3)_2]]Cl$, 7. Two grams (8.5 mmol) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]]$ was dissolved in 50 mL of medium petroleum ether in a three-necked flask fitted with a nitrogen bubbler system and a gas inlet. Gaseous HCl was bubbled into the solution for 5 min. Precipitation of a yellow solid occurred immediately. After stirring for 1 h, with occasional addition of HCl, the precipitate was collected, washed with ether, and dried to give a nearly quantitative yield of crude product. Recrystallization from hot acetonitrile/ether gave 1.60 g (70%) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2NH(CH_3)_2]]Cl$ as fine, yellow crystals. Anal. Calcd for $C_{10}H_{14}NFeClO_2$: C, 44.24; H, 5.20; N, 5.16; Fe, 20.57; Cl, 13.06. Found: C, 44.47; H, 5.39; N, 5.28; Fe, 20.32; Cl, 12.77.

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_3]]I$, 8. A 2.0-g portion of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]]$, 8.5 mmol, was dissolved in 25 mL of medium petroleum ether and 1.8 g (12.8 mmol) of methyl iodide was added. Precipitation of solid began immediately. After stirring for 5 h at room temperature, the product was collected and washed with ether. The crude salt was recrystallized from hot acetonitrile/ether to yield 2.20 g (69%) of bright yellow-orange crystals. Anal. Calcd for $C_{11}H_{16}NFeIO_2$: C, 35.05; H, 4.28; N, 3.71; Fe, 14.81;

I, 33.66. Found: C, 34.76; H, 4.28; N, 3.71; Fe, 14.75; I, 32.81.

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2BH_3)]$, 9. A 1.50-g (6.4 mmol) portion of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]]$ was dissolved in 25 mL of THF in a three-necked flask connected to a nitrogen bubbler system. The flask was cooled to −78 °C and a stoichiometric amount of BH_3:THF in THF was added by syringe. The reaction mixture was stirred and allowed to warm slowly to room temperature. After an hour at room temperature, the solvent was evaporated under vacuum. The crude product was taken up in ether, petroleum ether was added, and solvent was evaporated to yield bright yellow crystals which were collected, washed with petroleum ether, and dried, yield 1.05 g (66%). Anal. Calcd for $C_{10}H_{16}FeNO_2B$: C, 48.26; H, 6.47; N, 5.63; Fe, 22.44. Found: C, 47.83, 48.22; H, 6.35, 6.22; N, 5.70, 5.98; Fe, 21.84, 21.46.

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2(BF_3)]]$, 10. A three-necked flask equipped with a dropping funnel and a nitrogen inlet was charged with 1.0 g (4.25 mmol) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]]$ in 25 mL of ether. A stoichiometric amount of boron trifluoride etherate, 0.60 g, was mixed with ether in the dropping funnel. After cooling the flask to −78 °C the boron trifluoride etherate solution was added over 25 min. Solid precipitated immediately. After warming to room temperature, the mixture was stirred for several hours. Petroleum ether was added to precipitate more of the product, which was then collected, washed, and dried. Recrystallization from hot THF/petroleum ether gave 0.58 g (45%) of a yellow orange solid. Anal. Calcd for $C_{10}H_{13}NFeO_2BF_3$: C, 39.65; H, 4.33; N, 4.62; Fe, 18.44. Found: C, 39.37; H, 4.44; N, 4.57; Fe, 18.15.

Reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]]$ with CH_3COCl. Under nitrogen, a 2.00-g (8.5 mmol) portion of $(\eta^5\text{-}C_6H_5)Fe(CO)_2(\eta^1\text{-}CH_2N(CH_3)_2)$ was dissolved in 50 mL of hexane in a 100-mL three-necked flask. A dropping funnel containing 20 mL of hexane and 0.70 mL (about 0.77 g, 9.00 mmol) of acetyl chloride (fractionally distilled from *N,N*-dimethylaniline) was attached to the third neck of the flask. The flask was cooled to −78 °C with a dry ice bath and the solution of acetyl chloride added over a 15-min period. A yellow solid formed in the cold reaction mixture. After maintaining the reaction mixture at −78 °C for an additional 45 min, it was allowed to warm slowly to room temperature. A small quantity (0.05 g) of insoluble grey-brown powder was removed by filtration; comparison of the infrared spectrum of the filtrate with that of the starting solution indicated complete consumption of the starting material. The solvent was evaporated from the filtrate to yield a dark brown-red gel, whose NMR spectrum showed it to consist of an equimolar mixture of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2Cl)$ and *N,N*-dimethylacetamide. The product was kept at −10 °C for several days, which caused it to separate into an orange solid and a clear oil. The latter was removed by washing the solid twice with small amounts of cold hexane. After drying in vacuum, 1.40 g (73%) of a yellow orange solid, identified as $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}CH_2Cl)$ by comparison of its infrared and NMR spectra with that of an authentic sample, was obtained.

Reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]]$ with Trifluoroacetic Anhydride. A three-necked flask containing a solution of 1.50 g (6.4 mmol) of $[(\eta^5\text{-}C_5H_5Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]]$ in 30 mL of hexane was placed under nitrogen and cooled at −78 °C. The cold solution was treated with 1.64 g (7.8 mmol) of trifluoroacetic anhydride, added slowly with a gas tight syringe. An immediate color change from yellow-orange to blood red was observed. The reaction mixture was stirred for 2 h at −78 °C. The infrared spectrum of the reaction mixture showed no absorptions from the starting material and the appearance of two new, terminal carbonyl absorptions as well as two new bands between 1710 and 1780 cm^{-1}. The flask was warmed slowly to room temperature and the solvent evaporated to yield an orange oil. The residue was chromatographed on a silica gel column with hexane. The leading orange band yielded 1.20 g (62%) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2OC(O)CF_3]]$, **11**, as an orange oil. Elution with ether/hexane of the second red band yielded a small amount of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$. Anal. Calcd for $C_{10}H_7FeF_3O_4$: C, 39.51; H, 2.32. Found: C, 39.76; H, 2.29.

Reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]]$ with Trifluoromethanesulfonic Anhydride. A solution of 1.50 g (6.4 mmol) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]]$ in 40 mL of hexane contained in a three-necked flask was cooled to −78 °C, and 1.84 g (6.5 mmol) of trifluoromethanesulfonic anhydride was slowly added to the cold solution with a gas-tight syringe. Immediately upon addition, a yellow powdery solid formed. The reaction mixture was stirred at −78 °C for 1 h, then warmed to room temperature, filtered, and the filtered solid washed with ether. The yellow powdery product was recrystallized from acetonitrile/ether to give 1.65 g, 90% of bright yellow crystalline $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]]SO_3CF_3$, **12**, identified on the basis of IR, NMR, and microanalytical data. Anal. Calcd for $C_{19}H_{20}Fe_2NSF_3O_7$: C, 39.68; H, 3.51; N, 2.44; S, 5.58. Found: C, 38.86; H, 3.45; N, 2.67; S, 6.11.

$[(\eta^5\text{-}C_5H_5)Fe(CO)[\eta^2\text{-}CH_2N(CH_3)_2]]$, 13. A solution of 3.0 g of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[\eta^1\text{-}CH_2N(CH_3)_2]]$ in 90 mL of ether was placed in a quartz tube equipped with a water-cooled cold finger and a nitrogen inlet. The tube was irradiated with light from a 200-W Hanovia mercury lamp. Infrared spectra of samples of the reaction mixture indicated rapid disappearance of the starting material, with complete reaction after about 3.5-h irradiation. The solution was transferred to a round-bottomed flask, the ether evaporated, and the residue extracted with several portions of medium petroleum ether. After filtration the solvent was evaporated, producing an oily material that sublimed in vacuo at 55 °C to yield 1.65 g (63%) of sublimed material as long, thin, dark red needles. Anal. Calcd for $C_9H_{13}NFeO$: C, 52.41; H, 6.30; N, 6.73; Fe, 26.85. Found: C, 52.40; H, 6.29; N, 6.36; Fe, 26.29.

$[(\eta^5\text{-}C_5H_5Fe(CO)[(C_6H_5)P(CH_3)_2][\eta^1\text{-}CH_2N(CH_3)_2]]$, 14. A 1.0-g (4.8 mmol) portion of $[(\eta^5\text{-}C_5H_5)Fe(CO)[\eta^2\text{-}CH_2N(CH_3)_2]]$ was dissolved in 25 mL of THF and 0.76 g (5.5 mmol) of $(C_5H_5)P(CH_3)_2$ was added. The solution was stirred overnight after which the solvent and excess phosphine were removed under vacuum. An NMR spectrum of the resulting brown oil indicated nearly complete reaction, with only traces of the starting materials detectable. Attempts at crystallization of the product from THF/petroleum ether or ether either at −78 °C or by evaporation cooling were not successful. The identity of the compound was confirmed by its NMR spectrum.

$[(\eta^5\text{-}C_5H_5)Fe(CO)[(C_6H_5)_2P(CH_3)][\eta^1\text{-}CH_2N(CH_3)_2]]$, 15. Reaction of 0.60 g (2.9 mmol) of $[(\eta^5\text{-}C_5H_5)Fe(CO)[\eta^2\text{-}CH_2N(CH_3)_2]]$ with 0.70 g (3.5 mmol) of $(C_6H_5)_2P(CH_3)$ as described above also gave the desired compound as brown oil. All attempts at crystallization failed. The identity of the compound was confirmed by its NMR spectrum.

$[(\eta^5\text{-}C_5H_5)Fe(CO)[(C_6H_5)_2P(CH_3)][\eta^1\text{-}CH_2N(CH_3)_2\text{-}BF_3]]$, 16. A solution of 1.2 g (3.0 mmol) of $[(\eta^5\text{-}C_5H_5)Fe(CO)\text{-}[(C_6H_5)_2P(CH_3)][\eta^1\text{-}CH_2N(CH_3)_2]]$ in THF was treated with an excess of distilled boron trifluoride–etherate (0.60 g, 4.2 mmol) dissolved in 30 mL of 50:50 THF/ether. A solid formed after about 30 min. After the reaction mixture was stirred overnight, additional THF was added to dissolve the yellow solid and the solution was filtered. Part of the solvent was evaporated off and ether added. After further evaporation of solvent a yellow powdery solid was obtained. This solid was recrystallized by dissolution in acetonitrile, filtration of the solution, and evaporation of solvent until solid began to form. Crystallization was completed by cooling the mixture overnight at 0 °C. The supernatant was removed while cold and the well-formed orange crystals washed with ether and dried in vacuo: Yield 0.45 g (32%). A second crop was obtained by evaporation of the mother liquor. Anal. Calcd for $C_{22}H_{26}FeNOPBF_3$: C, 55.62; H, 5.52; N, 2.95; Fe, 11.76. Found: C, 55.18; H, 5.45; N, 2.92; Fe, 11.14.

Infrared measurements were made whenever possible on cyclohexane solutions by using 0.05- or 0.1-mm cells with NaCl windows and a Perkin-Elmer 521 or 621 spectrophotometer. Spectra shown in Figure 2 were obtained with a scan speed of 50 cm^{-1}/min and a linear 10× scale expansion. Calibration of each spectrum was made using indene. Compounds not soluble in cyclohexane were examined in THF or CH_3CN. Variable temperature spectra were obtained by using an Air Products Cryotip low-temperature cell[33] in conjunction with the Perkin-Elmer 621 spectrophotometer. The cell path length was about 0.2 mm. Temperature measurements were made with a thermistor mounted on the tail stock of the refrigerator. Both methylcyclohexane and hexane were used as solvents with identical results.

Routine NMR spectra were obtained with a Varian T-60 spectrometer operated at ~28 °C. The data given in Table I were obtained from such spectra. Low temperature spectra were obtained with Varian HA-100 or JEOL JNM-PS-100 spectrometers.

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(14) Close examination of the spectrum of **5** shows that the higher energy absorption is asymmetric. Although the lower energy band shows little asymmetry, it is assumed to also be a composite absorption.

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(21) If R has no plane of symmetry, then three rotational isomers exist. This could result in six infrared absorption bands (three pairs) if all were resolved. We are not aware of an example in which these have been resolved.

(22) By using representative bond distances and angles from X-ray structures on $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CO_2H$[23] and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)]$,[24] the Fe–N distance is 2.8–2.9 Å in the undistorted molecule. By using the same distances and angles, the *N*-carbonyl carbon distance is ~2.6 Å. Carbonyl ligands are, of course, susceptible to nucleophilic attack and the possibility that an interaction between nitrogen and CO exists cannot be totally excluded. However, we do not see how two different species involving N–CO interactions could occur.

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Cyclopentadienylbis(ligand)nickel(I): Synthesis and Characterization, Including the X-ray Structure of η^5-Cyclopentadienyl-1,1′-bipyridylnickel(I). Observations on the Mechanism of Substitution of Nickelocene

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The chemistry of nickel in the formal 1+ oxidation state is very poorly defined at present. Although several complexes have been isolated,[1] many have resulted from fortuitous syntheses and most are poorly characterized with respect to structure and reactivity patterns. Nickel(I) species are potential intermediates in reactions that involve Ni(0) ⇌ Ni(II) conversions, but few efforts have been made to detect them. Evidence is slowly accumulating that indicates Ni(I) species participate in chemistry that is unrelated to their role in a Ni(0) ⇌ Ni(II) process. For example, various Ni(I) species are claimed to undergo oxidative–addition (to the 3+ state)[2] and to react with oxygen[3a] (to give an adduct) and olefins.[3b]

This communication is a preliminary report on the synthesis and characterization of Ni(I) complexes of formula $[(C_5H_5)NiL_2]$[4] (L = R_3P, R_2POR, $RP(OR)_2$, $P(OR)_3$; L_2 = diphos,[5] arphos,[5] bpy, *o*-phen) including the X-ray structure of CpNi(bpy). Our results indicate that these species are intimately involved in a number of reactions of cyclopentadienylnickel complexes. Two examples of this type of Ni(I) complex have been reported. Uhlig and Walther first isolated $CpNi[PhP(n\text{-}Bu)_2]_2$ according to reaction 3[6] and later from (2)[7] (Table I). More recently CpNiN(Ph)NNNPh was prepared from Cp_2Ni and PhN_3.[8]

Each of the reactions listed in Table I produced an EPR active product, although when L was a phosphorus(III) ester the EPR signal decayed after a short time regardless of the method of preparation. The same EPR active products were obtained in several cases by electrochemical reduction of $[CpNiL_2]^+$ salts. Sample spectra are shown in Figure 1. Spectra of complexes that contain identical phosphorus ligands consist of 1:2:1 triplets except for the $PhP(OMe)_2$ and $P(OMe)_3$ complexes which give a doublet of doublets.[9,10] Superhyperfine splitting was not resolved in the

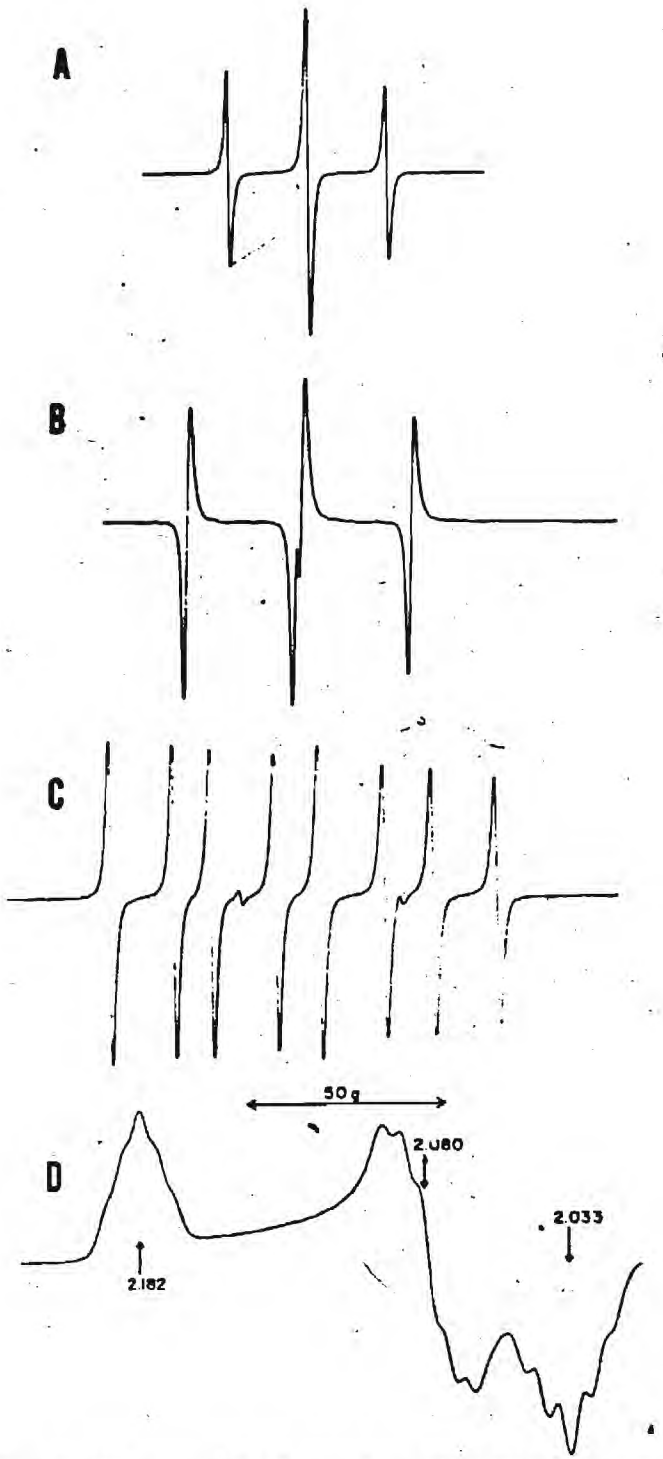

Figure 1. EPR spectra of $CpNiL_2$ Complexes. (A) CpNi(diphos): THF, 25 °C; $g = 2.068$, $A = 122$ G. (B) $CpNi[PPh(OMe)_2]_2$: toluene, 25 °C; $g = 2.052$, $A_1 = 170$ G, $A_2 = 180$ G. (C) CpNi(arphos): THF, 25 °C; $g = 2.075$, $A_P = 100$ G, $A_{As} = 170$ G. (D) CpNi(bpy): THF, −196 °C; $g_1 = 2.184$, $g_2 = 2.080$, $g_3 = 2.033$, $A_1 = 8.4$ G, $A_2 = 8.8$ G, $A_3 = 11.3$ G (from simulated spectrum).

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(4) Hereafter C_5H_5 will be abbreviated as Cp when the group is known or suspected to be bonded in pentahapto fashion.
(5) Diphos is $Ph_2PCH_2CH_2PPh_2$; arphos is $Ph_2AsCH_2CH_2PPh_2$.
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(9) The reason for the nonequivalence of the two donors in not known.
(10) Mixed ligand complexes result from reaction of $CpNiL_2$ with L′. The following complexes have been identified: $[CpNi[PhP(n\text{-}Bu)_2][P(OMe)_3]]$, $g = 2.057$, $A_{P_1} = 189$ G, and $A_{P_2} = 135$ G; $[CpNi[P(n\text{-}Bu)_3][P(OMe)_3]]$, $g = 2.055$, $A_{P_1} = 212$ G, and $A_{P_2} = 140$ G; $[CpNi[PhP(n\text{-}Bu)_2](CO)]$, $g = 2.036$ and $A_P = 150$ G. For comparison, the parameters of the precursor complexes are as follows: $PhP(n\text{-}Bu)_2$, $g = 2.076$, $A = 117$ G; $P(n\text{-}Bu)_3$, $g = 2.075$, $A = 125$ G; for the bis(trimethyl phosphite) complex, $g = 2.051$ and $A = 193$ and 208 G.

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Table I. Reactions Leading to Formation of $CpNiL_2$ Complexes

reactants	ligands and conditions[a,b]
(1) $(Ph_3P)_2NiCl + NaCp$	THF, room temperature
(2) $Cp_2Ni + L_4Ni$	L = Ph_3P; THF, 25 °C. L = $PhP(n\text{-}Bu)_2$; THF or hexane, 60 °C. L = diphos, $PhP(CH_3)_2$, Ph_2PCH_3, THF, 60 °C.
(3) $Cp_2Ni + 2L$ or L_2	L = $PhP(n\text{-}Bu)_2$, $P(n\text{-}Bu)_3$, PEt_3, bpy, *o*-phen, diphos; THF or hexane, 60 °C. L = Ph_2POMe, $PhP(OMe)_2$ (1%), $P(OMe)_3$; toluene, 25 °C.
(4) $CpNiL_2^+ + NaCp$	L = diphos (100%), PPh_3, $PhP(n\text{-}Bu)_2$, $P(n\text{-}Bu)_3$ (67%), Ph_2POMe (4%); THF, 25 °C.
(5) $L_2NiX_2 + NaCp$ X = Cl, Br	L = diphos (98%), bpy, arphos, PPh_3, $PhP(n\text{-}Bu)_2$, (92%), PMe_3, $PhPMe_2$, $P(n\text{-}Bu)_3$ (55%); THF; 25 °C.
(6) CpNiNO + excess L	L = $PhPMe_2$, $P(n\text{-}Bu)_3$; hexane or benzene, 50 °C.
(7) $[CpNiCO]_2$ + excess L[d]	L = $PhP(n\text{-}Bu)_2$, $P(n\text{-}Bu)_3$, $P(OMe)_3$; THF, 25 °C.
(8) $[CpNi(CH_2PPh_3)_2]^+ + 2L$	L = $P(OMe)_3$, $P(n\text{-}Bu)_3$; THF, 25 °C.

[a] All reactions were conducted under N_2 in a glove box or with appropriate glassware. EPR samples were prepared in the glove box. [b] Yields are highly variable as are stabilities of the products. Most reactions were not surveyed for yield; the yields indicated were obtained by comparison of the integral of the EPR spectrum taken on a filtered reaction mixture with that obtained for $Ti(acac)_3$ in a THF solution of known and comparable concentration. Since Ni(I) complexes of phosphorus(III) ester are unstable, the value given refers to the highest conversion seen in a given experiment. [c] Phosphines of the type Ph_2PR, as well as Ph_3P, yield $L_4Ni_{(s)}$ in hexane although very weak EPR signals due to the nickel(I) species were detectable for the green supernatant which contained unreacted nickelocene. Reactions conducted in THF were homogeneous, and strong EPR signals due to the Ni(I) complex were observed. [d] EPR signals corresponding to CpNi(CO)L were also detected for L = $P(OMe)_3$.[12] Ultimate products are $Cp_2Ni + Ni(CO)_2L_2$ (Ellgen, P. C. *Inorg. Chem.* 1971, *10*, 232).

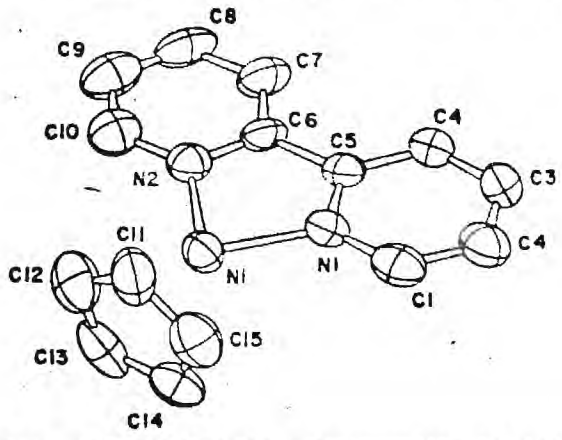


Figure 2. ORTEP drawing of CpNi(bpy). Hydrogen atoms are not shown; probability ellipsoids are shown at the 50% level. Numbering scheme applies to data in Tables 4–7 in the supplementary material.

isotropic spectra of the bpy and *o*-phen derivatives; however, the expected five-line patterns were observed for each *g* tensor component of anisotropic spectra (illustrated for the bpy complex in Figure 1D).[11] The hyperfine coupling patterns and *g* values are consistent with the presence of an $S = {}^1/_2$ complex ligated by two group 5 donors.

Although readily formed, the air-sensitive paramagnetic products were very difficult to isolate because of their high solubility and their tendency to decompose to Cp_2Ni and NiL_4, vide infra. However, CpNi(diphos) and CpNi(bpy) (Figure 2) as well as the previously reported $CpNi[PPh(n\text{-}Bu)_2]_2$ were isolated in analytically pure form.[12] Each of these dark-blue compounds has a magnetic moment[13] consistent with their formulation as d^9 complexes, and each had an isotropic EPR spectrum identical with that observed for the appropriate reaction mixtures listed in Table I. These observations strongly suggest that all of the EPR active products have the composition $CpNiL_2$ and contain nickel in the formal 1+ oxidation state.

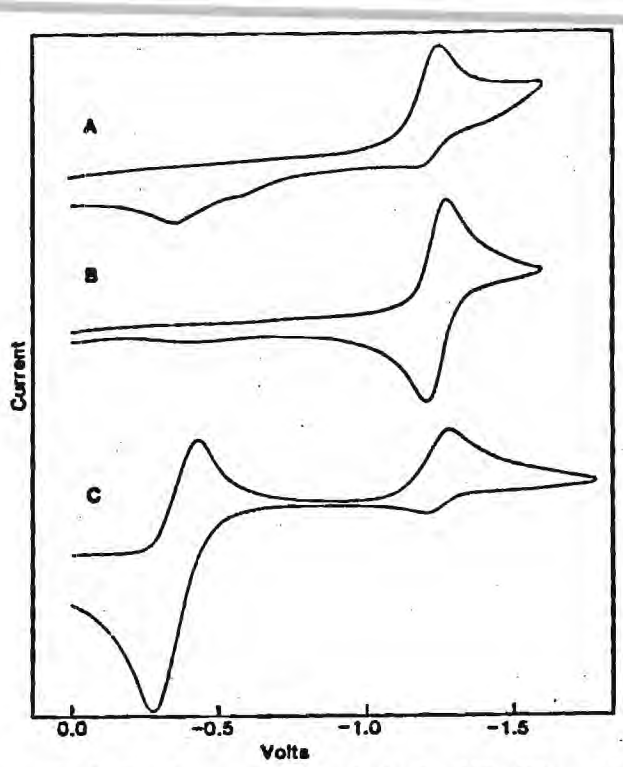


Figure 3. Cyclic voltammetry traces obtained at 200 mV/s on 0.1 M $(n\text{-}Bu)_4NBF_4/CH_3CN$ solutions vs. 0.1 M Ag^+/Ag reference. (A) 10^{-3} M $[CpNi(PPh_3)_2]PF_6$; (B) 10^{-3} M $[CpNi(PPh_3)_2]PF_6 + 10^{-2}$ M PPh_3; (C) 10^{-3} M $Cp_2Ni + 10^{-3}$ M $Ni(PPh_3)_4$.

Unfortunately, the EPR data provide no details concerning the mode of bonding of the cyclopentadienyl group to the nickel atom. By conventional electron counting, the complexes are 19 or 17 e^- systems depending upon whether the C_5H_5 moiety is bonded in η^5 or η^3 fashion. Uhlig and Walther tentatively suggested,[7] on the basis of infrared spectral data, that the cyclopentadienyl group in the $PhP(n\text{-}Bu)_2$ complex might be bonded in an η^3 manner. An X-ray structure determination[14] on the bpy complex

(11) CpNiN(Ph)NNNPh[t] also displays a rhombic EPR spectrum at −196 °C (THF–toluene) $g_1 = 1.97$, $g_2 = 2.01$, and $g_3 = 2.08$. Only g_2 shows superhyperfine splitting by the two nitrogen donors.

(12) The bpy complex was prepared by reaction 3 (Table I); 3–5-h reflux followed by filtration and subsequent evaporation of the THF solvent. Bpy/Ni ratios up to 3:1 were employed. The yield of dark blue-violet product was about 40%. The crystal of this complex chosen for X-ray analysis was obtained by evaporative cooling of a THF solution. The diphos complex was prepared by reaction 5. After a 2 h reaction time the THF solution was evaporated and the residue taken up in benzene and passed over a short alumina column. Concentration of the solution gave a blue amorphous solid (78%). The $PhP(n\text{-}Bu)_2$ complex was prepared by Uhlig's procedure[6] in isolated yields in the range 30–60%.

(13) The presence of one unpaired electron is indicated by the magnetic moments (μ_B) of the bpy and diphos complexes which were 1.69 and 1.76, respectively (obtained by the Evans NMR method). Uhlig and Walther found $\mu_B = 1.76$ for the $PhP(n\text{-}Bu)_2$ complex.

(14) Crystal data and details of data collection and refinement details are contained in Tables 2 and 3 (available as supplementary material). The structure was solved by Patterson, difference Fourier, and full-matrix least-squares techniques using the SHELX-76 program package and a CDC Cyber 76/6400 computer. Positional and anisotropic thermal parameters of nonhydrogen atoms were refined. Hydrogen atoms were included in calculated positions (carbon atoms sp^2 hybridization; C–H distances (1.08 Å) with refinement of isotropic thermal parameters. At convergence $R = 0.047$ with $R_w = 0.048$ for 1673 data with $F > 3\sigma(F)$. Data were not corrected for absorption. Tables 4–8 (available as supplementary material) contain final positional and anisotropic thermal parameters for nonhydrogen atoms (Table 4), final positional and isotropic thermal parameters for hydrogen atoms (Table 5), interatomic distances and angles (Table 6), least-squares planes (Table 7) and structure factor tables (Table 8).

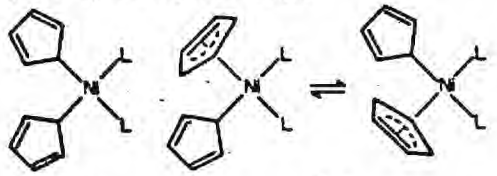
shows that the C_5H_5 group is pentahapto. A drawing of the molecule is shown in Figure 3. Nickel–nitrogen atom distances are equal [1.955 (3) and 1.958 (4)Å], and the cyclopentadienyl ligand is planar[15] with nickel–carbon distances ranging from 2.17 (4) to 2.22 (4) Å.[16] The nickel atom is 1.844 Å from the plane of the cyclopentadienyl carbon atoms which is at an angle of 89.1° to the plane defined by the nickel and bipyridyl ligand atoms. There is no indication of an η^3 interaction for the cyclopentadienyl group of the type found for one ring in $(C_5H_5)_2W(CO)_2$,[17] and CpNi(bpy) should be considered as a 19 e⁻ species, at least in the solid state.

The reaction of nickelocene with phosphorus ligands is a useful synthetic procedure for preparing NiL_4 complexes. Our results indicate that $CpNiL_2$ complexes are intermediates in these reactions. The stability of the nickel(I) complexes varies considerably; EPR signals for phosphine and nitrogen donor complexes persisted without change in intensity for long periods of time once equilibrium was established, whereas the complexes of phosphorus(III) esters were transients with NiL_4 complexes as the ultimate products. A kinetic study by Werner et al.[13] established the rate law $-d[Cp_2Ni]/dt = k[Cp_2Ni][L]^2$ for the production of $Ni[P(OEt)_3]_4$ in dioxane. It was assumed that the intermediate (clearly $CpNiL_2$) reacted with additional ligand to produce NiL_4 and a second C_5H_5 radical.[19] Although this pathway cannot be excluded, several observations indicate that an alternative pathway involves cyclopentadienyl transfer between two $CpNiL_2$ molecules to yield Cp_2Ni and NiL_4.

The existence of a ring-transfer process is particularly evident for $[CpNi(PPh_3)_2]$. A mixture of Cp_2Ni and $Ni(PPh_3)_4$ (1:1) gave a dark brown solution[20] identical with that obtained from the reaction of $(Ph_3P)_3NiCl$ with NaCp, (both in THF) and an identical 1:2:1 triplet in the EPR spectrum. Cyclic voltammetry scans on $[CpNi(PPh_3)_2]PF_6$ showed a cathodic wave at −1.25 V, a much smaller anodic wave at −1.18 V ($i_p^a/i_p^c < 0.6$), and an anodic wave at −0.35 V corresponding to nickelocene (Figure 3a). CV scans of a mixture of nickelocene and $Ni(PPh_3)_4$ showed the same irreversible process observed for the cationic complex (Figure 3c).[21] Thus nickelocene and the Ni(0) complex are in equilibrium with the Ni(I) complex and the disproportionation of Ni(I) is fast compared to the CV time scale. Addition of a 10-fold excess of triphenylphosphine to $[CpNi(PPh_3)_2]^+$ results in completely reversible electrochemical behavior (Figure 3b) and suggests that the formation of nickelocene proceeds via the 17 e⁻ species, $CpNiPPh_3$, which is formed by dissociation of triphenylphosphine.

Other $CpNiL_2^+$ salts undergo reduction when the potential range is from −1.1 to −1.7 V with varying degrees of reversibility. Anodic waves for one or more products were observed for irreversible cases. In some instances these included nickelocene, but in others it was not detectable.[22] Although both the Ph_2POMe and the $PhP(OMe)_2$ complexes showed reversible behavior, bulk electrolysis produced nickelocene and NiL_4.

Information concerning the mechanism of reduction of $[CpNiL_2]^+$ salts with NaCp (reactions 4 and 5) comes from the following experiment: $CpNi(diphos)^+$ was treated with 1.1 equiv of $C_5D_5^-$ (87% deuterated) in THF, and the resulting Ni(I) product was oxidized with I_2 to give $CpNi(diphos)^+$ in which the cyclopentadienyl ligand was 41% deuterated (determined by integration of the NMR spectrum). This result is consistent with the presence of an intermediate in which the two cyclopentadienyl ligands are bonded to the nickel atom and equilibrated through symmetry or a dynamic process, e.g.,

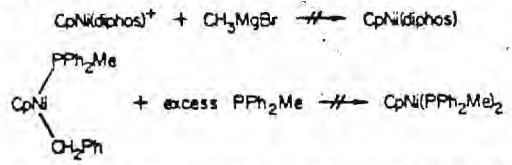


16 e⁻ 18 e⁻

It is not unreasonable to expect that the formation of $CpNiL_2$ from nickelocene occurs via the same type of intermediate.

The ylide complex, $[CpNi(CH_2PPh_3)_2]^+$, which was recently reported as the product of $Cp_2Ni + 2\ CH_2^-PPh_3^+$,[23] is one of the few examples of a product resulting from displacement of $C_5H_5^-$ by a neutral ligand.[24,25] Although only the PF_6^- and BPh_4^- salts were characterized by Booth,[23] we have isolated the cyclopentadienyl salt as the direct product of the displacement reaction and find that it reacts with phosphines to produce $CpNiL_2$ species. No EPR signal was observed for a monophosphine product, which suggests that reduction by the $C_5H_5^-$ anion does not occur until both ylide ligands are substituted. Cyclic voltammetry scans on $[CpNi(CH_2PPh_3)_2]PF_6$ (same conditions as given for Figure 3) showed that the complex was irreversibly reduced at ~−2.2 V but was reversibly *oxidized* with $E_{1/2} = -0.21$ V.

The diverse behavior of the nickelocene $CH_2^-PPh_3^+$ system compared to that of group 5 donors is consistent with the idea that π-bonding ligands stabilize lower oxidation states whereas they are destabilized by coordination of good σ donors. In fact, it is surprising to us that the cyclopentadienide anion functions as a reducing agent in any case if the primary oxidation product is C_5H_5 radical since ΔH_f for the radical is 42 kcal/mol greater than that of the anion (in the gas phase).[19] Anions such as $C_6H_5CH_2^-$ and CH_3^- do not function as reducing agents under similar conditions, e.g.,



It is not clear whether the nickel–σ-cyclopentadienyl bond is much lower in energy than other nickel–carbon σ bonds or if the effectiveness of the anion as a reducing agent is due to an anchimeric process involving the cyclopentadienyl double bonds.[26] This point as well as other reactions of these fascinating compounds are under study.

Acknowledgment. The combined support of the National Science Foundation and Research Corporation, which supplied funds for purchase of an inert atmosphere box in the early stages

(15) Maximum deviation from the least-squares plane defined by the five carbon atoms is 0.006 Å.

(16) For comparison, Cp_2Ni has a Ni–C distance of 2.196 (8) Å (Hedberg, L.; Hedberg, K. *J. Chem. Phys.* 1970, *53*, 1228) and the Ni–C(Cp) distances average 2.14 Å in $CpNi(PPh_3)Ar$ (Ar = C_6H_5 or C_6F_5) (Churchill, M. R.; O'Brien, T. A. *J. Chem. Soc. A* 1969, 266; 1968, 2970).

(17) W–C distances for the η^3 ring were 2.28, 2.40, and 2.98 Å. Huttner, G.; Brintzinger, H. H.; Bell, L. G.; Friedrich, P.; Bejenke, V., Neugebauer, D. *J. Organomet. Chem.* 1978, *145*, 329.

(18) Werner, H.; Harder, V.; Deckelmann, E. *Helv. Chim. Acta* 1969, *52*, 1081.

(19) Direct evidence for the formation of C_5H_5 radical has not been obtained.

(20) The blue-violet color observed for other phosphine derivatives is apparently masked by the intense color of $Ni(PPh_3)_4$.

(21) $Ni(PPh_3)_4$ should also be electroactive in this potential range; Kochi reports $E_{1/2}$ for $Ni(PPh_3)_4$ (10^{-3} M in CH_3CN) to be −1.1 V (corrected to 0.1 M Ag/Ag) (Tsou, T. T.; Kochi, J. K.; *J. Am. Chem. Soc.* 1979, *101*, 6319). However, we have observed poorly defined waves and low diffusion currents for this complex at concentrations $<10^{-3}$ M.

(22) There are a number of possibilities for "decomposition" products including the formation of analogues to the di-μ-(cyclopentadienyl)bis(ligand)dipalladium(I) complexes reported by Werner (Werner, H.; Kraus, H. *J. Chem. Soc., Chem. Commun.* 1979, 814) and Suzuki (Suzuki, K.; Jindo, A. *Inorg. Chim. Acta* 1980, *44*, L37). CV studies on $[CpNiL_2]^+$ in the presence of added L have not been made for ligands other than PPh_3.

(23) Booth, B. L.; Smith, K. G. *J. Organomet. Chem.* 1979, *178*, 361.

(24) The only other example known to us is the claim that Cp_2Ni yields $[Ni(NH_3)_6](C_5H_5)_2$ in $NH_3(l)$. Behrens, J.; Meyer, K. *Z. Naturforsch. B* 1966, *21B*, 489.

(25) $C_5H_5^-$ is displaced by other anions such as $C_3H_5^-$ (to give $CpNi(\eta^3\text{-}C_3H_5)$: McClellan, W. R.; Hoehn, H. H.; Cripps, H. N.; Muetterties, E. L.; Howk, B. W. *J. Am. Chem. Soc.* 1961, *83*, 1601) and $Li_2C_5H_6$ [to give bis(pentalenyl)dinickel]: Katz, T. J.; Acton, N. *J. Am. Chem. Soc.* 1972, *94*, 3281].

(26) Labinger has reported reactions of $CpFe(CO)_2(\eta^1\text{-}C_3H_5)$ with phosphorus ligands that do not occur with other alkyl analogues. Labinger, J. A. *J. Organomet. Chem.* 1977, *136*, C31. Fabian, B. D.; Labinger, J. A. *J. Am. Chem. Soc.* 1979, *101*, 2239.

of this work, is gratefully acknowledged. E.K.B. appreciates many helpful and stimulating discussions with Professors E. M. Burgess and C. L. Liotta.

Supplementary Material Available: Tables of crystal data, data collection and refinement details, final positional and anisotropic thermal parameters for nonhydrogen atoms, final positional and isotropic thermal parameters for hydrogen atoms, interatomic distances and angles, least-squares planes, and structure factors (12 pages). Ordering information is given on any current masthead page.

without distillation. One gram of the mixture was heated with 0.1 g of cuprous bromide at 55 °C for 2.5 h with magnetic stirring. The sample was filtered on a sintered glass funnel and its composition determined by gas chromatography. This analysis showed that the mixture was 11% 8 and 89% 13.

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Registry No. 1, 19008-94-7; 2, 19008-97-0; 3, 19008-98-1; 4, 19008-95-8; 5, 19008-96-9; 6, 56758-73-7; 7, 79152-78-6; 8, 79152-79-7; 9, 3043-33-2; 10, 2327-98-2; 11, 27301-54-8; 12, 27301-53-7; 13, 7544-00-5; 14, 17074-99-6; 15, 79172-18-2; 16, 5876-76-6; 17, 3355-30-4; 18, 79152-80-0; 19, 622-76-4; 20, 33598-22-0; 1-phenyl-2-butyn-1-ol, 32398-66-6; trimethyltin chloride, 1066-45-1; triphenyltin chloride, 639-58-7; triethyltin chloride, 994-31-0; 2,4-dinitrobenzenesulfenyl chloride, 528-76-7; chlorine, 7782-50-5; bromine, 7726-95-6.

Organometallic Chemistry of Carbon–Nitrogen Multiple Bonds. 3. Reaction of Tris(triphenylphosphine)platinum(0) with Dimethylmethyleniminium Chloride. X-ray Structures of the Products $[(Ph_3P)PtCH_2N(CH_3)_2CH_2N(CH_3)_2(Cl)]Cl$ and *cis*-$[(Ph_3P)Pt[CHN(CH_3)_2]Cl_2]$

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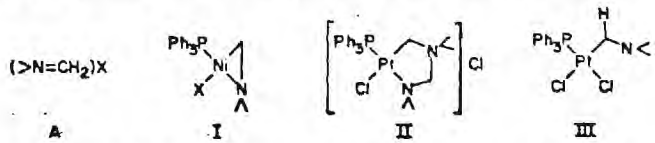
Tris(triphenylphosphine)platinum(0) reacts with $[(CH_3)_2N{=}CH_2]Cl$ in THF to yield $[(Ph_3P)PtCH_2N(CH_3)_2CH_2N(CH_3)_2(Cl)]Cl$ (A) which may be considered as a complex of the bidentate ylide ligand $^-CH_2N^+(CH_3)_2CH_2N(CH_3)_2$. When heated in acetonitrile, A converts quantitatively to the carbene complex *cis*-$[(Ph_3P)Pt[CHN(CH_3)_2]Cl_2]$ (B) ($\nu_{C=N}$ = 1611 cm^{-1}) and $(CH_3)_3N$. This decomposition is dependent upon the presence of a coordinating anion as shown by the stability of the BF_4^- salt of A in CH_3CN. The results of single-crystal X-ray structures for A and B are presented. Crystal data are as follows. A: space group $P2_1/c$, a = 13.86 (1) Å, b = 8.933 (2) Å, c = 19.52 (1) Å, β = 98.65 (6)°, Z = 4, ρ_{calcd} = 1.791 g cm^{-3}, ρ_{exptl} = 1.77 g cm^{-3}. B: space group $R\bar{3}$, a = 20.400 (8) Å, α = 117.68 (3)°, Z = 6, ρ_{calcd} = 1.763 g cm^{-3}, ρ_{exptl} = 1.77 g cm^{-3}. A has Pt–L distances of P, 2.223 (2) Å, Cl, 2.362 (2) Å, N, 2.134 (4) Å, and C, 2.017 (5) Å. The Pt–C distance is the shortest presently known for an sp^3 carbon (without fluorine substituents) bonded trans to chlorine. B has Pt–L distances of P, 2.220 (2) Å, Cl(1), 2.347 (3) Å, Cl(2), 2.345 (3) Å, and C, 1.96 (1) Å. The dihedral angle between the carbene and coordination planes is 84°.

Introduction

An earlier publication dealt with the syntheses of $[(Ph_3P)Ni(X)[\eta^2\text{-}CH_2N(CH_3)_2]]$ (X = Cl, Br, I) (I) and the single-crystal X-ray structure of the chloro complex.[1] These complexes were prepared from $(Ph_3P)_4Ni$ or $(Ph_3P)_2Ni(C_2H_4)$ and dimethylmethyleniminium halides (A) and represented the first phase of our investigations of the organometallic chemistry of iminium salts.[2] The analogous reaction of $(Ph_3P)_4Pt$ with A (X = Cl) produced a complex that analyzed for Ph_3P, Pt, and iminium salt in the ration 1:1:2. The NMR and infrared spectra of this



compound did not help in the assignment of a structure. A single crystal X-ray structure shows that the complex has structure II, which may be considered as a complex of the bidentate ylide ligand $^-CH_2N^+(CH_3)_2CH_2N(CH_3)_2$. This compound converts to the carbene complex III and $(CH_3)_3N$ under mild conditions. The single-crystal X-ray structure of the carbene complex indicates that it has the cis stereochemistry. The chemistry of these complexes, details of the structures, and a discussion of the probable mechanisms of reactions of iminium salts with zero-valent d^{10} metals are the subjects of this paper.

Experimental Section

Preparative work was conducted in a Vacuum Atmospheres glovebox under a nitrogen atmosphere. Solvents were distilled from drying agents under a nitrogen atmosphere. Dimethylmethyleniminium chloride[3] and $(Ph_3P)_3Pt$[4] were prepared by literature methods.

$[(Ph_3P)PtCH_2N(CH_3)_2CH_2N(CH_3)_2(Cl)]Cl$. A suspension of 0.5 g (0.4 mmol) of $(Ph_3P)_3Pt$ and 0.15 g (1.6 mmol) of $[(CH_3)_2N{=}CH_2]Cl$ in 50 mL of THF was stirred overnight. The off-white solid was collected by filtration and extracted on the frit with three 5-mL portions of CH_2Cl_2. Addition of ether to the extracts gave the product as a microcrystalline off-white material. Yield: 0.2 g or 78%. Anal. Calcd for $PtC_{24}H_{31}N_2Cl_2P$: C, 44.71; H, 4.85; N, 4.35; Cl, 11.00. Found: C, 42.89, 42.88, 43.56; H, 4.99, 4.97, 4.50; N, 4.41, 4.24; Cl, 10.87. Crystallographic quality crystals were obtained by evaporation of an acetonitrile solution of the complex.

$[(Ph_3P)PtCH_2N(CH_3)_2CH_2N(CH_3)_2Cl]BF_4$. Metathesis to the fluoroborate was accomplished by dissolving 1.25 g of the chloride in 125 mL of acetonitrile and adding a 10% excess of $NaBF_4$. After precipitated NaCl was removed the volume was reduced to half and the solution was stored at −3 °C for overnight; a second crop of NaCl was removed by filtration. After the volume

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Table I. Crystal Data for $[(Ph_3P)PtCH_2N(CH_3)_2CH_2N(CH_3)_2(Cl)]Cl$ (A) and *cis*-$\{(Ph_3P)Pt[CHN(CH_3)_2]Cl_2\}$ (B)

	A	B
mol wt	644.48	585.38
dimens, mm	0.08 × 0.25 × 0.40	0.40 × 0.40 × 0.60
space group	$P2_1/c$	$R\bar{3}$
cell constants		
a, A	13.86 (1)	20.400 (8)
b, A	8.933 (2)	
c, A	19.52 (1)	
α, deg		117.68 (3)
β, deg	98.65 (6)	
no. of reflctns used to determine cell constants and their 2θ limits, deg	15 $4 < 2\theta < 19$	15 $15.9 < 2\theta < 34.75$
Z	4	6
ρ_{calcd}, g cm^{-3}	1.791	1.763
ρ_{expdl},[a] g cm^{-3}	1.77	1.77

[a] By flotation in carbon tetrachloride/1,2-dibromoethane.

Table II. Data Collection and Refinement Details for $[(Ph_3P)PtCH_2N(CH_3)_2N(CH_3)_2(Cl)]Cl$ (A) and *cis*-$\{(Ph_3P)Pt[CHN(CH_3)_2](Cl_2)\}$ (B)

	A	B
diffractometer	Syntex $P2_1$	
monochromator (Bragg 2θ angle, deg)	graphite (12.2)	
radiation, A	Mo K$\bar{\alpha}$, 0.71069	
take-off angle, deg	6.75	
scan method	θ–2θ	
scan speed, min/max, deg min^{-1}	3.9/29.3	2.02/29.3
scan width, deg	2.0	
bkgd/scan time ratio (TR)[a]	1.0	
no. of standards	3[b] (97)	
(monitoring freq, no. of reflctns)		
2θ limits of data, deg	$4 < 2\theta < 50$	
h,k,l	$-h,0,0 \rightarrow +h,+k,+l$	$-h,-k,0 \rightarrow +h,+k,+l$: $\lvert h\rvert \leq l$, $\lvert k\rvert \leq l$
no. of data	4682	5845
no. of data used in final refinement	3316[c]	3784[d]
no. of data/no. of variables	12.2	25.1
μ,[e] cm^{-1}	64.85	63.97
$R = (\Sigma \lvert \lvert F_o\rvert - \lvert F_c\rvert \rvert)/(\Sigma \lvert F_o\rvert)$ (function minimized = $\Sigma(\lvert F_o\rvert - \lvert F_c\rvert)^2$)	0.024	0.047
R_w	0.023[f]	0.049[g]

[a] Background counts measured before (BG1) and at the end (BG2) of the scan. Intensities determined from total scan (CT) and background (BG) counts by $I = CT - TR(BG1 + BG2)$. $\sigma_I = [CT + (TR)^2(BG1 + BG2)]^{1/2}$. $F_o = (I/Lp)^{1/2}$ where Lp is the Lorentz and polarization correction. [b] Standard reflections were as follows. A: 0,0,8; 0,2,0; 7,0.0. B: 0,0,5; 0,5,0; 5,0,0. [c] $I > 3\sigma_I$. [d] $F > 3\sigma_F$; $\sigma_F = \sigma_I/2(F)(Lp)$. [e] Data were corrected for absorption by an empirical method based on ψ scans of reflections near $\chi = 90°$; average $I_{max}/I_{min} = 2.9$ for A and 1.39 for B. [f] $R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w(\lvert F_o\rvert)^2]^{1/2}$; $w = 4I/\sigma_I$. [g] $R_w = [\Sigma(\lvert F_o\rvert - \lvert F_c\rvert)(w^{1/2})/[\Sigma(\lvert F_o\rvert)(w^{1/2})]$; $w = n/(\sigma_F^2 + mF^2)$ in the final cycle. n was 2.86 and m was 5.1×10^{-4}.

of the filtrate was reduced to ca. 25 mL, about 10 mL of ether was added and the solution again stored at −3 °C overnight. The white crystalline fluoroborate salt was collected, washed with ether, and dried in vacuo. Anal. Calcd for $PtC_{24}H_{31}N_2PClBF_4$: C, 41.43; H, 4.49; N, 4.03. Found: C, 41.35; H, 4.52; N, 4.02.

$[(Ph_3P)Pt[CHN(CH_3)_2]Cl_2]$. An acetonitrile solution of $[(Ph_3P)PtCH_2N(CH_3)_2CH_2N(CH_3)_2(Cl)]Cl$ was heated at reflux for 10 min. After the solution cooled, the volume was reduced under vacuum to give white crystals of the product, which were collected, washed with ether, and dried in vacuo. Two modifications were obtained in separate preparations. One of these showed a single ν_{CN} at 1611 cm^{-1} whereas the other showed two bands at 1611 and 1622 cm^{-1} (solid state, Nujol mull). The exact conditions leading to a predictable formation of a given modification were not determined. Anal. Calcd for $PtC_{21}H_{22}NPCl_2$: C, 43.09; H, 3.79; N, 2.39. Found: C, 42.34; H, 3.93; N, 2.30. Crystals for X-ray data collection of the form having only the 1611-cm^{-1} infrared stretch were grown by addition of ether to an acetonitrile solution of the complex followed by cooling at −3 °C overnight.

Solution and Refinement of the Structures of $[(Ph_3P)PtCH_2N(CH_3)_2CH_2N(CH_3)_2(Cl)]Cl$ (A) and $[(Ph_3P)Pt[CHN(CH_3)_2](Cl)]$ (B). Crystal data are given in Table I and certain details of data collection and refinement in Table II. All computations were done on a CDC Cyber 70/74 computer system.

In the case of A the position of the platinum atom was determined from a Patterson synthesis and after three cycles of least-squares refinement of the scale factor and platinum coordinates $R = 0.319$. A difference Fourier map revealed the chlorine and phosphorus positions. These were included for three cycles of least-squares refinement in which the coordinates and isotropic thermal parameters of all atoms were allowed to vary ($R = 0.195$). A subsequent difference Fourier map revealed the positions of all carbon and nitrogen atoms. Inclusion of these atoms in the refinement gave $R = 0.103$ after three cycles. At this point the Pt, Cl, and P atoms were refined anisotropically for three cycles ($R = 0.059$). Hydrogen atom positions for all nonmethyl carbons were calculated by assuming sp^2 or sp^3 geometry as appropriate. The position of at least one hydrogen atom attached to each methyl carbon was determined from a difference Fourier map, and positions of the remaining ones were calculated. All hydrogen atom positions were block refined for two cycles after which their coordinates and thermal parameters were held constant. All nonhydrogen atoms were then refined anisotropically to convergence at $R = 0.024$ ($R_w = 0.023$).

Programs used included Zalkin's FORDAP Fourier summation program, Ibers NUCLS5 modification of the Busing–Martin–Levy ORFLS full-matrix least-squares program, the Busing–Martin–Levy ORFFE function and error program, and various locally written programs. For structure factor calculations the scattering factors for nonhydrogen atoms were taken from Cromer and Waber's

tabulation;[5] and those for hydrogen were Stewart's.[6] Scattering factors for Pt, P, and Cl were corrected for the real and imaginary anomalous dispersion components by using the dispersion factors given by Cromer.[7] Positional and thermal parameters of nonhydrogen atoms obtained in the last least-squares cycle are given in Table III. Tables of hydrogen atom positions and structure factors have been deposited.

The structure of B was solved by direct methods. The position of the platinum atom was located via the *E* map showing the highest probability statistics and its positional parameters, isotropic thermal parameter, and the scale factor were subjected to three cycles of least-squares refinement. $R = 0.235$ (all computations utilized Sheldrick's Shelx-76 program package). A subsequent difference Fourier map revealed the positions of all nonhydrogen atoms. After three cycles of least-squares refinement of all positional and isotropic thermal parameters, the Pt, P, and Cl atoms were refined anisotropically for three additional least-squares cycles. At this point a difference Fourier map did not reveal any hydrogen atom positions; therefore, these were included in subsequent cycles of refinement in their calculated positions by assuming sp^2 or sp^3 hybridization of the carbon atoms as appropriate, and thermal parameters of each group (phenyl, methyl, etc.) of hydrogen atoms were treated as a unit. Least-squares refinement of hydrogen atom thermal parameters, positional and isotropic thermal parameters of phenyl group carbon atoms, and positional and anisotropic thermal parameters of the other nonhydrogen atoms was continued to convergence at $R = 0.047$ and $R_w = 0.049$. In the final cycle the thermal parameter of the C(3) hydrogen atom unit was fixed at 0.15 as it had grown steadily in previous cycles.

Scattering factors were taken from the current source;[8] those for all atoms except hydrogen were corrected for real and imaginary anomalous dispersion components.[9] Positional and thermal parameters of nonhydrogen atoms obtained in the last least-squares cycle are given in Tables IV and V. Tables of hydrogen atom positions and structure factors have been deposited.

Results

Preparation and Spectral Characterization of $[(Ph_3P)\overline{PtCH_2N(CH_3)_2N(CH_3)_2Cl}]^+$ Salts and $\{(Ph_3P)Pt[CHN(CH_3)_2]Cl_2\}$. By analogy with our earlier work, in which we found that $(Ph_3P)_4Ni$ or $(Ph_3P)_2Ni(C_2H_4)$ reacted with excess $[(CH_3)_2N{=}CH_2]Cl$ in THF to give soluble $\{(Ph_3P)Ni[\eta^2\text{-}CH_2N(CH_3)_2]Cl\}$,[1] we expected a similar product from $(Ph_3P)_3Pt$. Instead, a THF-insoluble product that contained 2 equiv of iminium salt was consistently obtained, even from reactions involving 1:1 ratios of reactants. The infrared spectrum of this material contained no absorptions for vinylic CH or for C=N but gave no other information that could be used in structure assignment. The NMR spectra obtained initially varied with the solvent used and were not entirely reproducible in a given solvent, but they were not consistent with the presence of *N,N,N',N'*-tetramethylethylenediamine which was initially considered as a possibility since reductive carbon–carbon bond formation can be achieved with certain nickel(0) reagents.[10] Poor reproducibility of the NMR spectrum was ultimately traced to the instability of the chelate complex and the presence of carbene complex in the NMR samples. Carefully handled and purified samples of both the chloro and fluoroborate complexes gave reproducible spectra (data and assignments are given in Table VI) which are consistent with the structure of the cation as determined by X-ray diffraction (vide infra). The assignments of the different methylene and methyl resonances are based on the relative sizes of the Pt coupling constants. It should be noted that the coordinated CH_2 resonance (δ 3.26) is at somewhat higher field than the methine resonance in *trans*-$\{(o\text{-}CH_3C_5H_4N)Pt[CH(NC_5H_4\text{-}o\text{-}CH_3)CH_2CH_2Ph]Cl_2\}$ which is at δ 5.6[11] and the $^2J_{PtH}$ value is somewhat smaller (53 vs. 112 Hz). Since only one quaternary ammonium methyl resonance is detected, the chelate ring must undergo inversion at a rate that is rapid on the NMR time scale.

When $[(Ph_3P)\overline{PtCH_2N(CH_3)_2N(CH_3)_2(Cl)}]Cl$ is heated in acetonitrile, quantitative conversion to *cis*-$\{(Ph_3P)Pt[CHN(CH_3)_2]Cl_2\}$ and $(CH_3)_3N$ occurs as shown by the NMR spectrum of the reaction mixture. This complex was easily isolated by evaporation of the acetonitrile. Its infrared spectrum contains a band at 1611 cm^{-1} for the C–N stretching absorption, which is the range observed for other secondary carbene complexes.[12] The ^1H NMR spectrum contains methyl resonances at δ 2.85 (singlet) and 3.52 ($^4J_{PtH} = 12$ Hz) and the carbene carbon hydrogen at δ 9.81 ($^2J_{PtH} = 22$ Hz, $^3J_{PH} = 4$ Hz). Phenyl proton resonances are multiplets at δ 7.44 and 7.73. The observation of two distinct methyl signals indicates that rotation about the C–N bond is slow as previously noted by Clark[12] for a number of other secondary carbene platinum complexes. On the basis of the detectable coupling to platinum, the low-field methyl resonance is assigned to the group trans to platinum. The small value of $^3J_{PH}$ for the hydrogen attached to the carbene carbon is consistent with the cis orientation of phosphine and carbene ligands found for the solid-state material.

The only reasonable pathway for conversion of the chelate complex to the carbene must involve chelate ring cleavage and the formation of free iminum cation which serves as an hydride abstracter. It seemed likely that either the chloride counterion or the polar solvent might promote dissociation of the amino group from the platinum atom. The fluoroborate salt of the chelate complex was synthesized to test for a counterion effect. In fact, the fluoroborate salt of the chelate complex did not yield a detectable quantity of carbene complex when heated in acetonitrile and we conclude that the chloride counterion rather than solvent is most important for the conversion. (The BF_4^- salt of the chelate complex does decompose in hot acetonitrile but at a much lower rate than the conversion of the chloride salt to carbene—products were not identified.) Although the conversion of the chloride salt to carbene is rapid in CH_3CN, it is much slower in $CHCl_3$. This may be a result of poor solvation of the iminum cation in this medium since formation of a neutral dichloro complex should be favored by the less polar solvent.

Description of the Structure of $[(Ph_3P)\overline{PtCH_2N(CH_3)_2CH_2N(CH_3)_2(Cl)}]Cl$. The crystal structure of $[(Ph_3P)\overline{PtCH_2N(CH_3)_2CH_2N(CH_3)_2(Cl)}]Cl$ consists of four-coordinate cations and noninteracting chloride anions. The cation (see Figure 1 for an ORTEP drawing) is four-coordinate and contains the unique chelating ligand $^-CH_2N^+(CH_3)_2CH_2N(CH_3)_2$ with triphenylphosphine coordinated trans to the dimethylamino function. Selected interatomic distances and angles are given in Table VII.

Although the cation can be loosely characterized as having a square-planar arrangement of ligands about the

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Table III. Final Positional and Anisotropic Thermal Parameters[a] (with Esd's) for Nonhydrogen Atoms of $[(Ph_3P)\overline{PtCH_2N(CH_3)_2CH_2N(CH_3)_2(Cl)}]Cl$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	−0.15419 (1)	0.31602 (2)	0.429869 (9)	0.02249 (9)	0.02218 (9)	0.02349 (9)	0.0013 (1)	0.00651 (5)	0.0003 (1)
Cl(1)	−0.09756 (9)	0.2439 (2)	0.54532 (6)	0.0405 (7)	0.0391 (6)	0.0272 (6)	0.0087 (6)	0.0049 (5)	0.0038 (5)
Cl(2)	0.1625 (1)	0.4505 (2)	0.24348 (8)	0.0423 (8)	0.0551 (9)	0.0564 (9)	−0.0032 (7)	0.0142 (7)	−0.0010 (8)
P	−0.30022 (8)	0.3904 (1)	0.45035 (6)	0.0236 (6)	0.0247 (6)	0.0258 (6)	0.0019 (5)	0.0063 (5)	0.0015 (5)
N(1)	−0.0150 (3)	0.2615 (5)	0.4025 (2)	0.029 (2)	0.024 (2)	0.033 (2)	0.004 (2)	0.010 (2)	0.003 (2)
N(2)	−0.0944 (3)	0.3930 (5)	0.2990 (2)	0.028 (2)	0.032 (2)	0.027 (2)	0.001 (2)	0.008 (2)	0.005 (2)
C(1)	0.0110 (4)	0.1016 (4)	0.4180 (3)	0.047 (3)	0.029 (3)	0.044 (3)	0.012 (2)	0.019 (3)	0.006 (2)
C(2)	0.0644 (3)	0.3544 (6)	0.4400 (3)	0.021 (2)	0.053 (4)	0.043 (3)	−0.005 (2)	−0.000 (2)	−0.007 (3)
C(3)	−0.0207 (3)	0.2797 (5)	0.3267 (3)	0.027 (2)	0.030 (3)	0.032 (3)	0.000 (2)	0.010 (2)	0.001 (2)
C(4)	−0.0634 (4)	0.5487 (6)	0.3192 (3)	0.042 (3)	0.025 (3)	0.051 (3)	−0.004 (2)	0.010 (3)	0.008 (3)
C(5)	−0.1077 (4)	0.3799 (7)	0.2218 (3)	0.041 (3)	0.065 (4)	0.022 (3)	0.004 (3)	0.009 (2)	0.007 (3)
C(6)	−0.1869 (4)	0.3541 (6)	0.3271 (3)	0.029 (2)	0.039 (3)	0.026 (2)	−0.002 (2)	0.012 (2)	0.001 (2)
C(7)	−0.3026 (3)	0.5931 (5)	0.4598 (2)	0.021 (2)	0.023 (3)	0.032 (3)	0.003 (2)	0.002 (2)	0.001 (2)
C(8)	−0.3328 (4)	0.6628 (6)	0.5156 (3)	0.038 (3)	0.028 (3)	0.044 (3)	0.003 (2)	0.012 (2)	−0.001 (2)
C(9)	−0.3201 (4)	0.8144 (8)	0.5248 (3)	0.058 (3)	0.037 (3)	0.054 (3)	0.005 (3)	0.011 (3)	−0.009 (3)
C(10)	−0.2797 (4)	0.8977 (6)	0.4786 (4)	0.046 (3)	0.023 (3)	0.068 (4)	0.006 (2)	0.007 (3)	0.004 (3)
C(11)	−0.2535 (4)	0.8322 (7)	0.4214 (4)	0.052 (3)	0.031 (4)	0.068 (4)	0.003 (3)	0.025 (3)	0.009 (3)
C(12)	−0.2633 (4)	0.6794 (7)	0.4121 (3)	0.050 (3)	0.035 (4)	0.048 (4)	0.010 (3)	0.022 (3)	0.012 (3)
C(13)	−0.3419 (3)	0.3157 (6)	0.5274 (2)	0.024 (2)	0.027 (2)	0.030 (2)	0.006 (2)	0.009 (2)	−0.002 (2)
C(14)	−0.2954 (3)	0.3539 (5)	0.5927 (3)	0.025 (2)	0.035 (3)	0.028 (2)	0.000 (2)	0.002 (2)	−0.001 (2)
C(15)	−0.3263 (4)	0.2955 (6)	0.6509 (3)	0.032 (2)	0.045 (3)	0.033 (3)	0.010 (3)	0.002 (2)	0.003 (3)
C(16)	−0.4029 (4)	0.1945 (7)	0.6449 (3)	0.050 (3)	0.041 (3)	0.039 (3)	0.005 (3)	0.019 (2)	0.010 (3)
C(17)	−0.4491 (4)	0.1550 (6)	0.5807 (3)	0.045 (3)	0.038 (4)	0.045 (3)	−0.011 (2)	0.018 (2)	−0.002 (2)
C(18)	−0.4196 (4)	0.2159 (5)	0.5218 (3)	0.038 (3)	0.031 (3)	0.031 (3)	−0.003 (2)	0.011 (2)	−0.002 (2)
C(19)	−0.3976 (3)	0.3381 (5)	0.3823 (2)	0.032 (2)	0.030 (3)	0.022 (2)	−0.003 (2)	0.011 (2)	−0.001 (2)
C(20)	−0.4833 (3)	0.4180 (6)	0.3679 (3)	0.027 (2)	0.038 (3)	0.034 (3)	0.003 (2)	0.006 (2)	0.003 (2)
C(21)	−0.5613 (4)	0.3624 (7)	0.3219 (3)	0.037 (3)	0.058 (4)	0.037 (3)	0.003 (3)	0.000 (2)	0.008 (3)
C(22)	−0.5530 (4)	0.2285 (8)	0.2908 (3)	0.038 (3)	0.068 (5)	0.037 (3)	−0.021 (3)	−0.002 (2)	0.000 (3)
C(23)	−0.4685 (4)	0.1467 (6)	0.3044 (3)	0.041 (3)	0.044 (4)	0.041 (3)	−0.016 (2)	0.009 (2)	−0.013 (2)
C(24)	−0.3901 (4)	0.2010 (6)	0.3500 (3)	0.040 (3)	0.033 (3)	0.033 (2)	−0.004 (2)	0.014 (2)	0.001 (2)

[a] The form of the expression defining the thermal ellipsoids is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Table IV. Final Positional and Thermal Parameters (with Esd's[a]) for Anisotropically Refined Atoms of *cis*-{$(Ph_3P)Pt[CHN(CH_3)_2](Cl)_2$}

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt	0.19964 (4)	0.12937 (4)	0.43050 (4)	0.0282 (2)	0.0301 (2)	0.0310 (2)	0.0267 (2)	0.0254 (2)	0.0256 (2)
Cl(1)	0.2220 (3)	0.2361 (3)	0.5751 (3)	0.073 (2)	0.058 (2)	0.068 (2)	0.054 (2)	0.065 (2)	0.061 (2)
Cl(2)	0.1411 (4)	0.1746 (4)	0.3514 (4)	0.090 (2)	0.087 (2)	0.083 (2)	0.079 (2)	0.072 (2)	0.082 (2)
P	0.2683 (2)	0.0996 (2)	0.5170 (2)	0.027 (1)	0.027 (1)	0.030 (1)	0.025 (1)	0.026 (1)	0.024 (1)
N	0.268 (1)	0.101 (1)	0.333 (1)	0.070 (7)	0.087 (8)	0.073 (7)	0.074 (7)	0.067 (7)	0.069 (7)
C(1)	0.177 (1)	0.040 (1)	0.306 (1)	0.042 (6)	0.048 (6)	0.043 (6)	0.041 (5)	0.037 (5)	0.038 (5)
C(2)	0.416 (1)	0.258 (2)	0.470 (2)	0.056 (8)	0.067 (9)	0.073 (9)	0.058 (8)	0.057 (8)	0.043 (8)
C(3)	0.239 (2)	0.018 (2)	0.232 (2)	0.13 (1)	0.13 (1)	0.11 (1)	0.11 (1)	0.11 (1)	0.11 (1)

[a] The form of the expression defining the thermal ellipsoids is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Table V. Final Positional and Isotropic Thermal Parameters for Phenyl Group Carbon Atoms of *cis*-{$(Ph_3P)Pt[CHN(CH_3)_2]Cl_2$}

atom	x	y	z	U, Å²
C(4)	0.4502 (9)	0.2771 (9)	0.7189 (9)	0.031 (2)
C(5)	0.568 (1)	0.395 (1)	0.786 (1)	0.036 (2)
C(6)	0.709 (1)	0.534 (1)	0.941 (1)	0.043 (2)
C(7)	0.726 (1)	0.554 (1)	1.025 (1)	0.053 (3)
C(8)	0.610 (1)	0.441 (1)	0.962 (1)	0.052 (3)
C(9)	0.470 (1)	0.300 (1)	0.807 (1)	0.045 (2)
C(10)	0.1484 (9)	−0.0220 (9)	0.4737 (9)	0.031 (2)
C(11)	0.159 (1)	−0.082 (1)	0.484 (1)	0.052 (3)
C(12)	0.070 (2)	−0.175 (2)	0.453 (2)	0.073 (4)
C(13)	−0.031 (1)	−0.210 (1)	0.411 (1)	0.055 (3)
C(14)	−0.040 (1)	−0.151 (1)	0.404 (1)	0.046 (2)
C(15)	0.046 (1)	−0.060 (1)	0.432 (1)	0.037 (2)
C(16)	0.2821 (9)	0.0204 (9)	0.4483 (9)	0.030 (2)
C(17)	0.414 (1)	0.102 (1)	0.530 (1)	0.042 (2)
C(18)	0.417 (1)	0.038 (1)	0.468 (1)	0.051 (3)
C(19)	0.282 (1)	−0.113 (1)	0.321 (1)	0.055 (3)
C(20)	0.152 (1)	−0.196 (1)	0.239 (1)	0.064 (3)
C(21)	0.148 (1)	−0.131 (1)	0.299 (1)	0.055 (3)

platinum, the donor–Pt–donor angles are considerably different from the ideal ones. There is a slight tetrahedral distortion as shown by the deviations of the ligating atoms from the least-squares plane defined by the equation $0.304X + 0.935Y + 0.180Z - 3.075 = 0$. i.e., Cl(1), −0.059 Å; C(6), −0.076 Å; P, 0.061 Å, and N, 0.074 Å. The Pt atom is 0.008 Å out of this plane. There are also deviations in the in-plane angles from the ideal 90°; the N(1)–Pt–C(6) angle is only 82.2° whereas the Cl(1)–Pt–P and P–Pt–C(6) angles are 95.10 (7) and 93.2 (1)°, respectively. All angles and distances in the chelate and triphenylphosphine ligands are in the expected ranges.

The Pt–C distance of 2.017 (5) Å extends the range previously found for sp^3 carbon (without fluorine substituents) bonded trans to chlorine. The lower limit of this range was previously defined by values of 2.08 (1) and 2.090 (4) Å occurring in *trans*-$(Ph_3P)_2Pt(Cl)R$ (R = CH_2CN[13] and η^1-allyl[14]), respectively, and 2.081 (6) and 2.079 (14) Å in *trans*-$(Ph_2PCH_3)_2Pt(Cl)R$ (R = CH_3[15] and $CH_2Si(CH_3)_3$[16]) respectively. Although it is tempting to suggest that the shorter Pt–C distance is a result of a stronger interaction between the electronegative carbon donor (compare the Pt–C distance of 2.002 (9) Å in *trans*-$[Pt(Ph_2PCH_3)_2(C_2F_5)Cl]$[15] with the value of the CH_3 derivative given above), it is also possible that the shorter bond is partially a result of the constraint placed on the system by the chelate ring.

The Pt–P bond distance at 2.223 (2) Å is shorter than

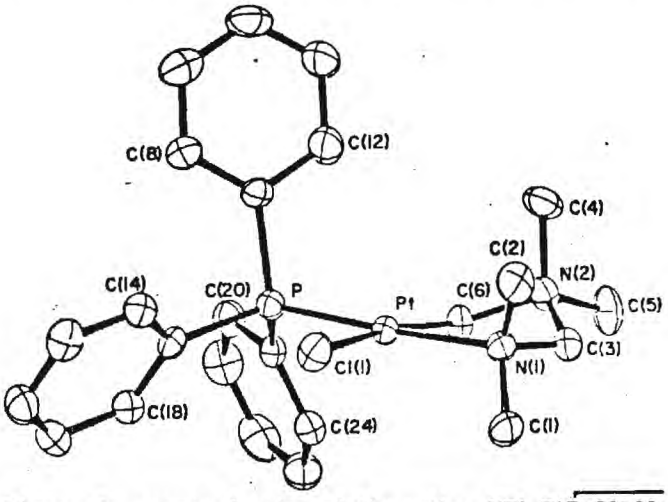

Figure 1. ORTEP drawing of the cation $[(Ph_3P)\overline{PtCH_2N(CH_3)_2CH_2N(CH_3)_2(Cl)}]^+$. Hydrogen atoms are not shown; probability ellipsoids are at the 50% level.

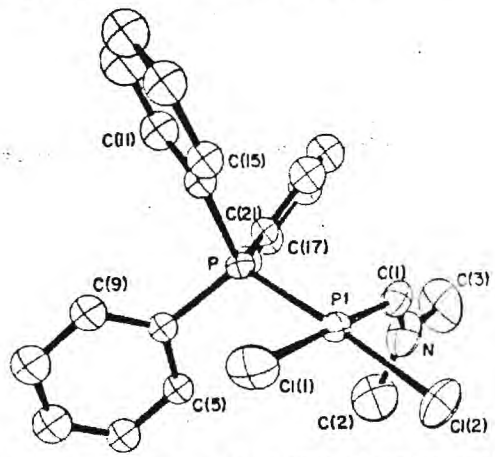

Figure 2. ORTEP drawing of *cis*-{$(Ph_3P)Pt[CHN(CH_3)_2]Cl_2$}. Hydrogen atoms are not shown; probability ellipsoids are at the 50% level.

distances recorded for *trans*-bis(phosphine)platinum(II) complexes (the minimum distance is about 2.29 Å), but this is not unexpected if there is a π component to the Pt–P bond since the trans amino group would not be competitive.

The Pt–Cl distance of 2.362 (2) Å is the same as that in *tran*-$[Pt(Ph_2PCH_3)_2(CF_3)Cl]$[15] within experimental error and is considerably shorter than those in other complexes where chlorine is bonded trans to sp^3 carbon donors.[14] As noted by Bennett et al., in regard to the CF_3 complex,[15] this is probably a result of an electrostatic dipolar effect induced by the electronegative carbon substituent.

Description of the Structure of *cis*-{$(Ph_3P)Pt$-

(13) Del Pra, A.; Zanotti, G.; Bombieri, G.; Ros, R. *Inorg. Chem.* 1979, *18*, 121.
(14) Kaduk, J. A.; Ibers, J. A. *J. Organomet. Chem.* 1977, *139*, 199.
(15) Bennett, M. A.; Chee, H.-K.; Robertson, G. B. *Inorg. Chem.* 1979, *18*, 1061.
(16) Jovanovic, B.; Manojlović-Muir, L.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* 1974, 195.
(17) Shomaker, V.; Waser, J.; Marsh, E. R.; Bergman, G., *Acta Crystallog.* 1959, *12*, 600.

Table VI. ^{1}H NMR Data for [(Ph$_3$P)PtCH$_2$N(CH$_3$)$_2$CH$_2$N(CH$_3$)$_2$(Cl)] and *cis*-{(Ph$_3$P)Pt[CHN(CH$_3$)$_2$]Cl$_2$}

compound	solvent, anion	chemical shifts (δ vs. Me$_4$Si) and coupling constants for proton types				
		a	b	c	d	e
	CD_3CN, BF_4^-	δ 3.14 ($^3J_{Pt-H}$ = 23 Hz, $^4J_{P-H}$ = 2.6 Hz)	δ 4.08 ($^3J_{Pt-H}$ = 28 Hz)	δ 3.09	δ 3.26 ($^2J_{Pt-H}$ = 53 Hz, $^3J_{P-H}$ = 1.52 Hz)	δ 7.47–7.69 (m)
	CD_3CN, Cl^-	δ 3.15 ($^3J_{Pt-H}$ = 24 Hz, $^4J_{P-H}$ = 2.8 Hz)	δ 4.28 ($^3J_{Pt-H}$ = 28 Hz)	δ 3.14	δ 3.30 ($^2J_{Pt-H}$ = 54 Hz, $^3J_{P-H}$ = 1.1 Hz)	δ 7.45–7.69 (m)
	$CDCl_3$	δ 2.85	δ 3.52 ($^3J_{Pt-H}$ = 12 Hz)	δ 9.81 ($^2J_{Pt-H}$ = 22 Hz, $^3J_{P-H}$ = 4 Hz)	δ 7.30–7.87 (m)	

Table VII. Interatomic Distances (Å) and Angles (Deg) for [(Ph$_3$P)PtCH$_2$N(CH$_3$)$_2$CH$_2$N(CH$_3$)$_2$(Cl)]Cl

Distances			
Pt-P	2.223 (2)	P-C(13)	1.817 (5)
Pt-Cl(1)	2.362 (2)	C(13)-C(14)	1.382 (7)
Pt-N(1)	2.134 (4)	C(14)-C(15)	1.375 (8)
Pt-C(6)	2.017 (5)	C(15)-C(16)	1.385 (8)
		C(16)-C(17)	1.366 (9)
N(1)-C(1)	1.492 (7)	C(17)-C(18)	1.386 (8)
N(1)-C(2)	1.481 (7)	C(18)-C(13)	1.390 (7)
N(1)-C(3)	1.478 (7)		
		P-C(19)	1.806 (5)
N(2)-C(3)	1.482 (7)	C(19)-C(20)	1.378 (7)
N(2)-C(4)	1.491 (7)	C(19)-C(24)	1.390 (7)
N(2)-C(5)	1.495 (7)	C(20)-C(21)	1.389 (8)
N(2)-C(6)	1.510 (6)	C(21)-C(22)	1.354 (9)
		C(22)-C(23)	1.371 (9)
P-C(7)	1.821 (5)	C(23)-C(24)	1.385 (8)
C(7)-C(8)	1.373 (7)		
C(8)-C(9)	1.374 (8)		
C(9)-C(10)	1.354 (9)		
C(10)-C(11)	1.357 (9)		
C(11)-C(12)	1.381 (8)		
C(12)-C(7)	1.383 (7)		
Angles			
Cl(1)-Pt-P	95.10 (7)	Pt-N(1)-C(3)	108.2 (3)
Cl(1)-Pt-N(1)	89.7 (1)	N(1)-C(3)-N(2)	111.8 (4)
P-Pt-C(6)	93.2 (1)	C(3)-N(2)-C(6)	106.9 (4)
N(1)-Pt-C(6)	82.2 (2)	N(2)-C(6)-Pt	108.9 (3)
P-Pt-N(1)	174.3 (1)	C(1)-N(1)-C(2)	106.8 (4)
Cl(1)-Pt-C(6)	170.9 (1)	C(4)-N(2)-C(5)	109.2 (4)

[CHN(CH$_3$)$_2$]Cl$_2$]. The crystal structure of the carbenoid complex consists of noninteracting, nearly planar molecules which have a cis stereochemistry. A perspective drawing is shown in Figure 2 and selected interatomic distances and angles and least squares planes are given in Table VIII.

In addition to being nearly planar, there are only minor deviations of the in-plane–Pt–donor angles from 90°. Likewise, the carbenoid ligand is highly planar. Interatomic angles associated with the carbene ligand are in agreement with the notion that bonding at carbon and nitrogen involve sp^2-hybrid orbitals although the Pt–Cl–N angle is somewhat large at 129.4 (8)°. This is not unexpected in view of the large difference in sizes of the substituents on carbon (Pt vs. H). The dihedral angle between the plane of the carbene ligand and the coordination plane is 84° which is within the range found for other Pt(II)–carbene complexes (70–90°).[18]

As described in the Experimental Section, some preparations of the carbene complex exhibited two C–N stretching absorptions in the solid state (1622 and 1611 cm^{-1}). Both samples gave a single C–N absorption in $CHCl_3$ solution at 1612 cm^{-1} and had identical NMR spectra in $CDCl_3$. X-ray diffraction data were collected on a crystal from a sample that exhibited two C–N stretching absorptions in the solid state, and the structure was solved.[19] Unfortunately, the structure exhibited some inexplicable differences in bond distances that suggested there might be imperfections in the crystal so that the structure has not been included here. However, it was apparent that the dihedral angle between the carbene and coordination planes differed in the two independent molecules in the unit cell (84° vs. 65°). Comparison of the infrared data for the two forms of the carbene complex

(18) (a) Manojlović-Muir, L.; Muir, K. W., *J. Chem. Soc., Dalton Trans.* **1974**, 2427. (b) Anderson, G. K.; Cross, R. J.; Manojlović-Muir, L.; Muir, K. W.; Wales, R. A. *Inorg. Chim. Acta* **1978**, *29*, L193.

(19) Crystal data: space group $C2/c$; a = 36.1 (3) Å, b = 9.07 (3) Å, c = 29.26 (4) Å, β = 109.42 (4)°, Z = 16. The crystal chosen for data collection was selected from a sample crystallized by cooling a saturated acetonitrile solution.

Scheme I

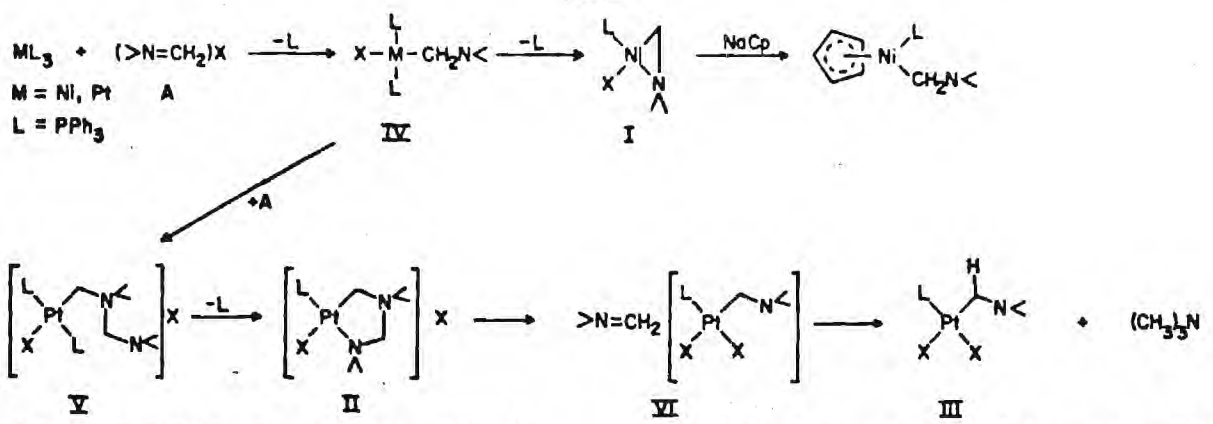

Table VIII. Selected Interatomic Distances (A) and Angles (Deg) and Least-Squares Planes for *cis*-{(Ph$_3$P)Pt[CHN(CH$_3$)$_2$]Cl$_2$}

Distances

Pt–Cl(1)	2.347 (3)	N–C(2)	1.42 (2)
Pt–Cl(2)	2.345 (3)	N–C(3)	1.46 (2)
Pt–C(1)	1.96 (1)	P–C(4)	1.818 (9)
Pt–P	2.220 (2)	P–C(10)	1.799 (9)
C(1)–N	1.25 (1)	P–C(16)	1.828 (9)

Angles

Cl(1)–Pt–Cl(2)	89.4 (1)	C(1)–N–C(2)	124 (1)
Cl(1)–Pt–C(1)	177.7 (3)	C(1)–N–C(3)	123 (1)
Cl(1)–Pt–P	90.1 (1)	C(2)–N–C(3)	113 (1)
Cl(2)–Pt–C(1)	88.4 (3)	Pt–P–C(4)	110.8 (3)
Cl(2)–Pt–P	176.8 (1)	Pt–P–C(10)	117.0 (3)
P–Pt–C(1)	92.2 (3)	Pt–P–C(16)	113.9 (3)
Pt–C(1)–N	129.4 (8)		

Least-Squares Planes[a]

$0.435X + 0.478Y + 0.763Z = 0.328$		$0.410X - 0.816Y + 0.407Z = 4.570$	
atom	dev, A	atom	dev, A
Pt	−0.021	N	−0.026
Cl(1)	−0.028	C(1)	0.010
Cl(2)	0.041	C(2)	0.008
P	0.042	C(3)	0.008
C(1)	−0.033		

[a] Least-squares planes were calculated by the method described in ref 17; all atoms have unit weight. Equations refer to orthogonal axes with the x axis coincident with a and z with c^*.

indicates that the smaller dihedral angle results in a higher C–N stretching frequency. Since bonding between a carbenoid ligand and the metal involves back-donation from filled metal orbitals to the carbene carbon p orbital, it would seem that the maximum interaction would occur for dihedral angles of 90 or 0°. In a coordinate system where the carbenoid ligand is on the x axis, these limiting cases would utilize the metal d_{xz} and d_{xy} orbitals, respectively, for the π interaction with carbene carbon p orbital. The latter situation is less favorable in nonchelated systems because of steric interactions between the groups attached to the carbene carbon and cis ligands attached to the metal. The reasons for the deviations of the dihedral angles from the ideal value in may of the structurally characterized complexes are not apparent. These deviations may be a result of crystal packing effects or possibly to a trade-off between Pt–C and C–N multiple bonding.

The Pt–C(1) and C(1)–N bond distances are 1.96 (1) and 1.25 (1) Å, respectively. Both of these distances are quite short and are consistent with the presence of substantial multiple bond character to each interaction. Table VIII lists the pertinent data for other *cis*-dichloroplatinum(II) carbene structures for comparison with the present data. The distances observed for our complex are generally comparable with those of earlier structures although the present C(carbene)–N distance is significantly shorter than those in which the carbene carbon is bonded to two heteroatoms. It is only slightly different from the C–O distance in the C(OEt)CH$_2$Ph complex.[18b] Although it might be expected, on the basis of the previous discussion of the dihedral angle, that the Pt–C and C–N distances should be inversely correlated, there are insufficient structural data on similar compounds to indicate the extent of any relationship between these parameters. It might be noted that a C(carbene)–N distance of 1.266 (15) Å was found for *trans*-{[PhP(CH$_3$)$_2$]$_2$Pt(CH$_3$)[C(CH$_3$)N(CH$_3$)$_2$]}PF$_6$.[21]

Both Pt–Cl distances in the present complex are the same, which suggests similar trans influences for the carbene and triphenylphosphine ligands. The Pt–P distance is typical of those for complexes in which the phosphine is bonded trans to chlorine; the phenyl C–C distances and internal angles are normal in every sense.

Discussion

All of the products derived from reaction of dimethylmethyleniminium halides and M(PPh$_3$)$_3$ (M = Ni, Pt) and the intermediates that we believe are involved in their formation are outlined in Scheme I. Species IV has not been detected for either Ni or Pt although it is the most likely product from the initial reaction. We assume that it results from electrophilic attack of the iminium cation on the metal. In the case of nickel, species I is irreversibly formed.[1] This complex can be converted to an η^1-CH$_2$N(CH$_3$)$_2$ form by treatment with sodium cyclopentadienide, but this rearrangement cannot be accomplished by the addition of phosphorus ligands.[1] We assume either that IV does not form with platinum or that I and IV are in rapid equilibrium and IV is removed by alkylation with a second equivalent of iminium salt (to give V initially). Conversion of IV to I in the case of nickel is apparently much faster than the alkylation reaction since no evidence for a product containing the chelate ligand was ever obtained.

We view the conversion of chelate complex II to carbene complex III as proceeding by substitution of the amino group by chloride followed by dealkylation and hydride abstraction by the liberated iminium cation. Hydride abstraction in a metal complex by an iminium salt has precedent. Fong and Wilkinson reported (CO)$_4$Fe[CHN(CH$_3$)$_2$] and (CO)$_5$Cr[CHN(CH$_3$)$_2$] as the products of reaction of [(CH$_3$)$_2$C=CH$_2$]I with Fe(CO)$_4^{2-}$ and Cr(CO)$_5^{2-}$,

(20) Badley, E. M; Muir, K. W.; Sim, G. A. *J. Chem. Soc., Dalton Trans.* 1976, 1930.

(21) Stepaniak, R. F.; Payne, N. C. *Inorg. Chem.* 1974, *13*, 797.

Table IX. Selected Structural Parameters in *cis*-[$Cl_2Pt(L)$(carbene)] Complexes

L	carbene	α,[a] deg	C_{sp^2}-X, Å	Pt-C, Å	Pt-Cl (trans to L), Å	Pt-Cl, Å	ref
PEt_3	C(OEt)NHPh	77	1.33 (2) O 1.33 (3) N	1.962 (18)	2.367 (7)	2.361 (5)	20
PMe_2Ph	C(OEt)CH_2Ph	85	1.283 (11)	1.920 (9)	2.355 (3)	2.375 (3)	19
PEt_3	CN(Ph)CH_2CH_2NPh	90	1.327 (11)	2.009 (13)	2.381 (3)	2.362 (3)	17
PPh_3	C(H)$N(CH_3)_2$	84	1.25 (1)	1.96 (1)	2.345 (3)	2.347 (3)	this work

[a] Dihedral angle between the carbene and coordination planes.

respectively.[22] These reactions apparently proceed via $(CO)_nM[\eta^1\text{-}CH_2N(CH_3)_2]^{1-}$, which reacts with a second equivalent of iminium salt. The fact that hydride abstraction has not been observed in neutral η^1-$CH_2N(CH_3)_2$ complexes is also consistent with the hypothesis of Cl^- involvement in the reaction of the chelate complex since proposed intermediate VI is then anionic.

We suggested earlier that the complexed $CH_2N(CH_3)_2$ moiety behaves much like the complexed allyl function.[2] This notion is further supported by the contrasting behavior of the allylnickel and -platinum complexes that are essentially analogous to I and II in the scheme. $[(\eta^3\text{-}C_3H_5)Pt(PPh_3)_2]Cl$ is apparently ionic in chloroform solution with a four-coordinate cation (assuming that the allyl group occupies two-coordination positions). However, the complex is fluxional (by NMR) in this medium even at −50 °C.[14] Since endo-exo proton interconversion in allyl complexes occurs via a σ-bonded allyl complex, this suggests that chloride ion is probably intimately involved in promoting the rearrangement (note that $[(\eta^3\text{-}C_3H_5)Pt(PR_3)Cl]$ complexes are stereochemically rigid). In fact, Kaduk and Ibers crystallized $[(\eta^1\text{-}C_3H_5)Pt(PPh_3)_2(Cl)]$ (as well as the ionic species) from a benzene–pentane solution.[14] In contrast, $[(\eta^3\text{-}C_3H_5)Ni(PPh_3)_2Cl]$ is five-coordinate and nonfluxional.[23] Thus, it appears that both η^3-allyl and η^2-iminium moieties are more strongly bonded to nickel than platinum (note that $\{(Ph_3P)_2Ni[\eta^2\text{-}CH_2N(CH_3)_2]\}^+ + Cl^-$ gives complex II).[1]

Work by Okawara and co-workers on oxidative-addition rections of $ClCH_2SCH_3$ with $(Ph_3P)_4M$ (M = Pd, Pt)[24,25] also suggests that η^2 forms of α-substituted alkyls are less stable for platinum than for the lighter group 8 elements. In both of these reactions *trans*-$[(Ph_3P)_2M(Cl)CH_2SCH_3]$ was formed (analogous to IV in the scheme) but the palladium complex was in equilibrium with $[(Ph_3P)Pd(\eta^2\text{-}CH_2SCH_3)Cl] + Ph_3P$. The η^2 complex can be isolated by removal of the dissociated phosphine. Removal of phosphine from the platinum complex gave $[(Ph_3P)Pt(\mu\text{-}CH_2SCH_3)Cl]_2$.

In view of Okawara's work, our failure to obtain complex IV with Pt is not easy to explain. However, the insolubility of the iminium salt and of the chelate complex in suitable solvents makes it difficult to make variations in reaction conditions. The fact that the chelate complex was obtained in reactions involving 1:1 ratios of $(Ph_3P)_3Pt$ and iminium salt suggests that formation of the chelate complex may be faster than oxidative-addition. Several attempts were made to prepare a η^1-$CH_2N(CH_3)_2$ complex using $LiCH_2N(CH_3)_2$[26] and Pt(II) starting materials but all failed in our hands.

Coupling of other unsaturates to give chelating ligands is well-known. To some extent the head-to-tail coupling of the iminium cations resembles the coupling reactions of $(CF_3)_2CO$ and $(CF_3)_2CNH$ performed by Stone and coworkers.[27] A large number of compounds of the type $L_2MXC(CF_3)_2YC(CF_3)_2$ (M = Ni, Pd, Pt; L = CNR, phosphorus or arsenic base; X = O, NH; Y = O, NH) were prepared, generally by addition of a second equivalent of unsaturate to a preformed π complex. It is believed, however, that these reactions occur via intermediates in which both unsaturated molecules are bonded in π fashion prior to C–N or C–O bond formation.

The process by which our chelating ligand is proposed to form is analogous to reactions of metal iminoacyls (M—CR=NR) with imidoyl halides in which the chelate complex M—C(R)=N(R)C(R)=NR is produced.[28-30]

Finally, it is interesting to note that although a much wider variety of bonding modes has been observed in phosphorus ylide complexes than is presently known for nitrogen ylides,[31] chelating forms of the former in which a neutral substituent serves as the second donor have not been prepared. One might expect, however, than an analogue of the nitrogen ylide chelate could be prepared from $[(CH_3)_2PCH_2P(CH_3)_3]^+$.[32]

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Registry No. A, 79328-81-7; B, 79328-82-8; $[(Ph_3P)PtCH_2N(CH_3)_2CH_2N(CH_3)_2Cl]BF_4$, 79328-84-0; $(Ph_3P)_3Pt$, 13517-35-6; $[(CH_3)_2N{=}CH_2]Cl$, 30354-18-8.

Supplementary Material Available: Tables of final positional and isotropic thermal parameters for hydrogens atoms (both structures) and a listing of observed and calculated structure factors (both structures) (33 pages). Ordering information is given on any current masthead page.

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